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CONSULTANT REPORT ON AN EVALUATION OF CATALYTIC CONVERTERS FOR CONTROL OF AUTOMOBILE EXHAUST POLLUTANTS

National Research Council

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September 1974

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CONSULTANT REPORT

of the

COMMITTEE ON MOTOR VEHICLE EMISSIONS COMMISSION ON SOCIOTECHNICAL SYSTEMS NATIONAL RESEARCH COUNCIL, ON AN EVALUATION OF CATALYTIC CONVERTERS FOR CONTROL OF AUTOMOBILE EXHAUST POLLUTANTS

SEPTEMBER 1974

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Waste Management
Office of Mobile Source Air Pollution Control
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CONSULTANT REPORT

to the

Committee on Motor Vehicle Emissions

Commission on Sociotechnical Systems

National Research Council

on

AN EVALUATION OF CATALYTIC CONVERTERS FOR CONTROL OF AUTOMOBILE EXHAUST POLLUTANTS

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Washington, D.C.

September 1974

NOTICE

This consultant report was prepared by a Panel of Consultants at the request of the Committee on Motor Vehicle Emissions of the National Academy of Sciences. Any opinions or conclusions in this consultant report are those of the Panel members and do not necessarily reflect those of the Committee or of the National Academy of Sciences.

This consultant report has not gone through the Academy review procedure. It has been reviewed by the Committee on Motor Vehicle Emissions only for its suitability as a partial basis for the report by the Committee.

The findings of the Committee on Motor Vehicle Emissions, based in part upon material in this consultant report but not solely dependent upon it, are found only in the Report by the Committee on Motor Vehicle Emissions of November 1974.

PREFACE

The National Academy of Sciences, through its Committee on Motor Vehicle Emissions (CMVE), initiated a study of automobile emissions-control technologies at the request of the United States Congress and the Environmental Protection Agency (EPA) in October 1973. To help carry out its work, the CMVE engaged panels of consultants to collect information and to prepare consultant reports on various facets of motor vehicle emissions control. This Consultant Report on An Evaluation of Catalytic Converters for Control of Automobile Exhaust Pollutants is one of five such consultant reports prepared and submitted to the Committee in connection with the Report by the Committee on Motor Vehicle Emissions of November 1974. The other consultant reports are:

Emissions and Fuel Economy Test Methods and Procedures, September 1974

Emissions Control of Engine Systems, September 1974

Field Performance of Emissions-Controlled Automobiles, November 1974

Manufacturability and Costs of Proposed Low-Emissions Automotive Engine Systems, November 1974

These five consultant reports are NOT reports of the National Academy of Sciences or its Committee on Motor Vehicle Emissions. They have been developed for the purpose of providing a partial basis for the report by the Committee as described more fully in the cover NOTICE.

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I. CONCLUSIONS AND RECOMMENDATIONS

A. CONCLUSIONS

The members of the Panel of Consultants found data concerning automobile emission-control catalysts presented by various companies to be in general agreement. Some of the major conclusions are listed below; each is discussed in further detail in the body of this report.

1. Hydrocarbon and carbon monoxide oxidation

a. For HC and CO oxidation, noble-metal catalysts (containing Pt, Pd, and/or Rh supported on oxide pellets or monoliths) have been demonstrated to meet the ultimate standards (0.4 and 3.4 g/mi, respectively) for 50,000 miles when run on EPA durability fuels.

b. No base-metal catalysts have demonstrated 50,000-mile durability, although some that have been promoted with as little as 0.01 wt% noble metal have exceeded 10,000 miles within standards.

c. Noble-metal oxidation catalysts increase the percent sulfur emitted as SO_3 from a baseline of less than 10% to a range of 15-60%, depending on the temperature and oxygen partial pressure; addition of an air pump increases SO_3/SO_2 exhaust ratios. The catalysts (especially in the pelleted form) have a capacity to retain relatively large quantities of sulfur oxides at low temperatures, but this adsorbed material is then "dumped" during high-temperature operation.

d. Since oxidation catalysts require lower operating temperatures than do thermal reactors, their use effectively "de-couples" engine performance and emission control by allowing the engine to be optimally tuned to give lower exhaust temperatures. When used optimally, oxidation catalysts could result in fuel-economy benefits as high as 20% over comparable 1974 model cars.

2. Nitrogen oxide reduction

a. NO_x control to the interim standards (e.g., 2.0 g/mi in California) can be achieved by engine adjustments alone without using catalysts.

b. Catalysts to meet the ultimate standards (0.4 g/mi for 50,000 miles), whether in dual-bed, triple-bed, or three-way systems, have not been demonstrated. Furthermore, due to uncertainties about the future NO_x standards, research is not being aggressively pursued by most manufacturers. Based on data available at this time, prospects for development of a suitable catalyst in the near future that will meet the 0.4 g/mi standard are not bright, although use of "high-temperature" base-metal catalysts on wire-mesh supports protected by an upstream oxygen scrubber show some promise <u>if</u> durability can be demonstrated.

c. Potential dual- (or triple-) bed low-temperature catalytic systems for NO_x control inherently involve fuel economy penalties, due to the requirement of fuel-rich operation, and necessarily place a heavier burden on the oxidation catalysts. Ammonia formation remains a problem for low- and intermediate-temperature NO_x catalysts. Among the low-temperature candidates only Ru catalysts are low-ammonia formers, but to date no satisfactory method has been demonstrated for stabilizing this noble metal against mass loss in an oxidizing atmosphere.

d. No catalyst has been developed that will decompose NO into its elements at moderate temperatures, even though such is thermodynamically possible. Furthermore, strong inhibition by oxygen makes such a development highly unlikely.

3. <u>Three-way catalyst systems</u>

It is possible to control all three pollutants simultaneously in a single converter. However, effective operation requires maintaining the fuel mixture to within ±0.1 air/fuel ratio units, a precision that has not been demonstrated with simple carburetion. Neither the catalyst nor the required oxygen sensor-feedback control system has demonstrated the necessary durability to meet the standards. The complexity and component reliability requirements for this system are quite stringent, and much more research will be necessary in order to make the three-way catalyst a viable approach to emission control.

4. Catalyst poisoning

The preponderance of evidence indicates that both NO_x and oxidation catalysts are unambiguously deactivated by the presence of compounds containing lead, bromine, and phosphorus at levels above those of EPA durability fuel and oil phosphorus specifications. Lead and phosphorus are "permanent" poisons, while bromine is a "temporary" poison. Synergistic effects between the various poisons may also be operative. With certain systems there are reports that lead alone does not poison the oxidation activity, but the members of the Panel of Consultants have been unable to resolve satisfactorily this apparent conflict on the basis of available data.

5. Abnormal driving modes

Early prototype catalytic converters reportedly exhibited a high incidence of catastrophic failure (burnout, cracking, attrition, etc.) when exposed to abnormal conditions due to ignition failure, vibration, accidental exposure to leaded gasoline, etc. Improvement in ignition systems, better catalyst packaging, and methods to avoid contamination with leaded fuels have greatly reduced these potential failure modes. Nevertheless, total ignition failure at high speeds (e.g., above 50 mph) almost certainly will result in temperatures sufficiently high to deactivate the catalysts permanently.

6. Materials availability and toxicology

a. All noble metals (Pt, Pd, Rh, Ru) must be imported, mainly from South Africa (and possibly the U.S.S.R.). Their use in catalytic converters will more than double the requirements for these metals in the U.S. While the supply is adequate to meet these new demands for several years, the price will undoubtedly increase and thus affect the cost of other items (e.g., electrical and telephone components) requiring their use.

b. The monolithic supports are all made by domestic suppliers, and production capacity has been expanded to meet the demands. Most of the beaded catalysts are supported on an alumina base. Currently, preference is given to an alumina manufactured by a French

company. No supply problems are anticipated by the domestic catalyst finishers who use this material.

c. The oxidation catalysts essentially eliminate the emission of polynuclear aromatics, olefins, and partially oxidized compounds, some of which are physiologically harmful and are active smog precursors. By requiring use of low-lead gasoline, the use of catalysts also will result in a decrease in the particulate emissions attributable largely to lead compounds.

d. Loss of noble metals from the exhaust systems is not a significant problem under normal operating conditions. During 50,000 mile tests, less than 10% of the catalytic material was lost. Furthermore, the members of the Panel of Consultants have seen no data to suggest emission of platinum or palladium in other than the metallic (nontoxic) form.

e. Technology for recycle of noble metals from aged automobile exhaust catalysts containing lead, various other metals, sulfur, refractory oxide support materials, etc. has not been proved in the absence of economic incentives. No tests have been conducted to explore the possibility of biological solubilization of noble metals in discarded converters, and thus it is impossible to assess the potential this may present for entry into the human food cycle through water contamination. However, the very small amounts of material (less than 0.1 oz/car) make such a possibility seem extremely remote. Moreover, more than 80% of all discarded automobiles are now reclaimed, and this figure is certain to increase as metals become more expensive.

f. While chemical techniques are known that can remove most lead from lead-poisoned catalysts in the laboratory and result in catalyst reactivation, field testing of these techniques on vehicles has not been done.

B. RECOMMENDATIONS

1. Poisoning by lead motor-mix components

Conflicting data have been received concerning the relative

poisoning characteristics of combustion products of ethylene dichloride, ethylene dibromide, and the alkyl lead compounds in the usual motor mix used for octane enhancement. Considering the extremely important implications of this uncertainty, we strongly recommend that a continuing, independent study be established to resolve this issue.

2. Environmental considerations

To assess the impact these catalytic converters may have on the environment, it is recommended that samples of soil and atmosphere near typical city, suburban, and freeway roads across the country be analyzed very carefully for Pb, S, P, noble metals, etc. before the end of 1974. These data will serve as a baseline for comparison with periodic measurements taken thereafter to monitor the increase (or decrease) in these components as the population of catalytic converter-equipped cars increases.

II. INTRODUCTION

The Panel of Consultants on Catalysts, established by the National Research Council's Committee on Motor Vehicle Emissions, was organized in January 1974. The charge to this Panel of Consultants was to assess the status of catalysts for automobile emission control and to estimate the future developments in catalytic converters, especially for NO_x removal. Geographically, the four consultant members came from widely dispersed areas (Houston, Chicago, Princeton, and San Francisco), and each has had several years' experience in the field of catalysis.

To gather data from which to draw conclusions, the members of the Panel of Consultants made site visits, either singly or in groups, to most domestic automobile producers and potential catalyst suppliers. Information from nondomestic automobile manufacturers was collected at a meeting in Washington, DC, at which many such companies were represented. Furthermore, the members of the Panel of Consultants used data from the open literature, material presented at technical meetings, suggestions from independent entrepreneurs, and intuitive assessments based on experience in catalysis when specific data were not available. Appendix A lists the companies visited; and Appendix B contains a typical questionnaire sent to each company prior to the visit.

With few exceptions, the members of the Panel of Consultants were cooperatively received by the various companies; two catalyst companies strongly discouraged visits, indicating they were unable to supply pertinent new information or that the questions asked did not pertain to their business. With the use of catalysts on light-duty motor vehicles now much more of a certainty (at least for oxidation), the companies were more willing to provide data on catalyst compositions, performance, durability, testing methods, etc. than occurred during a similar exercise two years ago. Moreover, there was more general agreement on many points than was apparent previously. This is due to more standardized, more accurate testing procedures that have evolved from identification and control of the significant variables that can influence the behavior of the catalysts.

Still the exact methods of catalyst preparation were seldom revealed, as these are generally regarded as proprietary secrets. Absence of such information did not seriously limit the conclusions, although in some instances it would have been informative to know the distribution of active components on the support, a factor that could influence the susceptibility of the material to poisoning.

Not everywhere is there complete agreement. One important disagreement between information from several automobile and oil companies arose in the effect of various ingredients in the lead-containing motor mix used in the fuel for octane enhancement. The data obtained appear contradictory, and the members of the Panel of Consultants have relied on their best judgment to resolve the conflict. While they are reasonably confident about their conclusions, more data are required in order to resolve this important issue with complete certainty.

The report begins with a general description of basic performance of the various systems, catalysts, and testing methods. The next chapter contains durability data and discusses factors that can lead to catalyst deactivation, e.g., thermal effects, chemical poisons, physical attrition, and pore blockage. The sulfate formation and possible toxicological effects of debris emitted from the converters are evaluated in the following chapter, and the last chapter summarizes mathematical modeling studies and what is known about the kinetics and mechanisms of the various reactions.

III. BASIC PERFORMANCE CHARACTERISTICS OF AUTO CATALYSTS

Consistent with the primary objective of this report to deal with catalysts for NO_x control, this chapter will treat only very generally the basic performance characteristics of oxidation catalysts and will focus most attention on the former.

A. Oxidation Catalysts

Carbon monoxide and hydrocarbons are eliminated through burning (or oxidation) to carbon dioxide and water. This can be accomplished either homogeneously at high temperatures in a thermal reactor or heterogeneously over a catalyst at much lower temperatures. Figure 1 gives some idea of the temperatures that are required to achieve various conversion levels in typical representatives of the two systems.[1]* Achieving the temperatures necessary for the thermal reactors requires "de-tuning" the engine in such a way as to increase the exhaust temperature above the normal 900-1100°F, and this is necessarily accompanied by a fuel-economy penalty and presents materials-corrosion difficulties in the reactor. On the other hand, the lower temperatures required by the catalytic system effectively "de-couple"[1] the exhaust purification and the engine parameters, a factor that should allow higher performance and more efficient operation of the automobile. Hence, there is considerable incentive to use catalytic converters for oxidation. It should also be noted in Figure 1 that whereas CO is the most difficult pollutant to remove in the thermal system, hydrocarbons pose the more serious problem over oxidation catalysts.

The only catalysts that are being considered for immediate use in automobiles for HC and CO control include the noble metals Pt, Pd, and Rh, either separately or in combination impregnated on pelleted or monolithic supports. The primary reasons these materials are favored over base metals are their resistance to sulfur poisoning, reluctance to form less active compounds through reaction with the support material, better light-off characteristics, and greater thermal stability to sintering.

*References are listed at the end of the report (page 105).

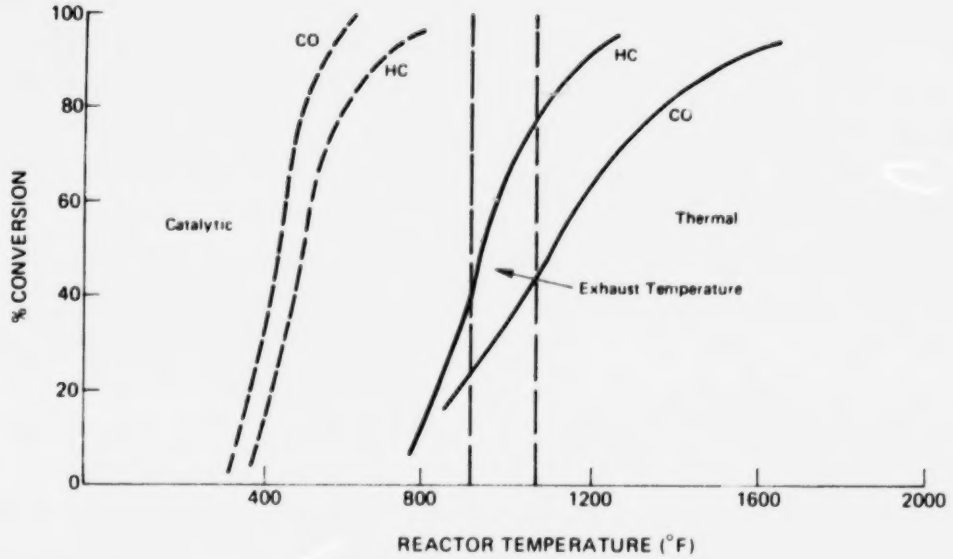

FIGURE 1a Comparison of Thermal Reactors and Catalytic Converters for Oxidation of HC and CO.

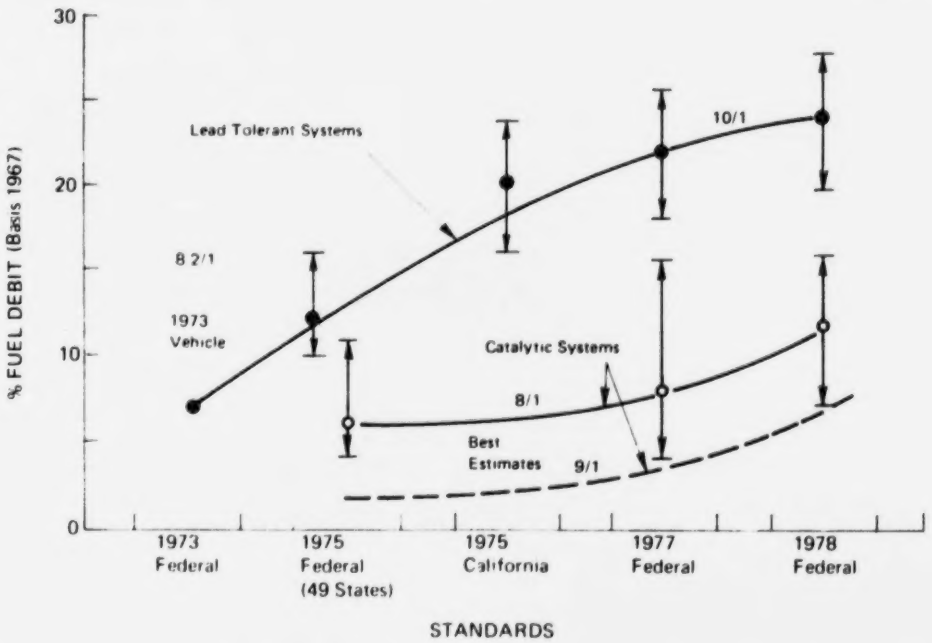

FIGURE 1b Predicted Fuel Economy of Various Emissions Control Systems with the Indicated Compression Ratio.

REF. 1

As will be discussed more fully in the next chapter, it is the lower activity for HC (than for CO) that limits the effectiveness of these catalysts. Thus, they must be designed primarily for HC removal, and the CO removal then requires only a fraction of the total catalyst. When a catalyst becomes poisoned, it is usually the HC activity that is first impaired. Furthermore, not all classes of HC are equally oxidized over noble metals, as may be seen in the Ford data in Table 1[2] for a pelleted catalyst that has been "aged" on an automobile for 12,000 miles. While fresh catalysts show higher overall activity, the relative ease of converting the various HC types always decreases in the order: acetylenes, aromatics, olefins and paraffins. Methane is the most difficult HC to oxidize, and the oxidation activity for paraffins increases with molecular weight. This is not thought to be a particularly severe problem, however, since methane shows almost no photochemical activity that results in smog formation. There have been suggestions that methane be removed from the HC standard, which would make the standard more easily met and would not have an adverse health effect. Such a relaxation would require modifications in the normal testing procedure and involve more sophisticated analytical equipment.

As long as fuel sulfur remains at the 0.03 wt% level, the Panel does not foresee the possibility of completely removing noble metals from the catalysts and still meeting the 50,000 mile durability requirement. It may be possible, however, to reduce the amount of noble metals by adding some base metals, but there is still considerable disagreement on this issue.

Oxidation catalysts also cause oxidation of SO_2 to SO_3, a problem that will be discussed in Chapter 5.

B. NO_x Reduction Catalysts

General considerations - In its application to automobile emission control, the catalytic conversion of NO_x has proceeded along two approaches: (1) the dual-bed system (and sometimes three-bed systems),

TABLE 1

EFFECT OF CATALYST ON EXHAUST GAS COMPOSITION

Cruise 30 - Vehicle 17-0-F - Indolene Clear Fuel
12,000 Miles

Compounds	PPM		%HC		HEW Reactivity	
	Before	After	Before	After	Before	After
Methane	45.4	45.7	8.5	33.4	0	0
Ethane	11.7	10.3	2.2	7.6	0	0
Butane	11.3	5.5	2.1	4.0	11	6
Isopentane	13.6	4.8	2.5	3.5	14	5
Total Paraffins	148.0	84.8	27.6	62.1	91	29
Total Acetylenes	50.7	0.5	9.5	0.4	0	0
Ethylene	97.5	20.0	18.2	14.7	390	80
Propylene	56.0	7.7	10.4	5.6	392	54
1-Butene, Isobutene	22.0	2.9	4.1	2.2	153	21
Total Olefins	223.6	34.6	41.7	25.4	1275	184
Benzene	14.2	3.6	2.6	2.7	0	0
Toluene	59.1	7.9	11.0	5.8	177	24
Total Aromatics	114.0	16.7	21.3	12.2	402	52
GRAND TOTAL	536	136.7	100.0	100.0	1768	265
Avg. Relative Reactivity					3.297	1.937

REF. 2

and (2) the three-way system. In the dual-bed system the combustion process involves net fuel-rich engine operation with passage of the exhaust gases first over a NO_x reduction catalyst that favors the formation of nitrogen rather than ammonia. Subsequently, air is introduced into the stream before it enters a second reactor containing an oxidation catalyst for conversion of hydrocarbons and carbon monoxide. Any ammonia formed in the first catalytic reactor will also tend to be oxidized back to NO_x in the oxidation reactor. To bring the catalytic system to its light-off temperature (warm-up), it has been found useful to operate the reduction catalyst briefly in an oxidizing mode by air injection on the upstream side of the first reactor. As a result, the reduction catalyst has to exhibit stability to a net oxidizing environment for short intervals (about 1 minute) during cold start-up of the engine.

In the three-way system the control of automobile exhaust is achieved by operating the engine near the stoichiometric air/fuel (A/F) ratio and employing a single catalyst for conversion of NO_x, HC, and CO. This catalytic system requires close control of the A/F ratio, a problem that has not been solved satisfactorily as yet. Consequently, the following discussion will deal primarily with NO_x reduction catalysts.

It is useful to classify the NO_x catalysts in terms of their respective temperature ranges for optimum performance.[2] On this basis the active components of the system fall into three categories:

(a) Low-temperature catalysts (Type A): This type of catalyst system contains ruthenium with and without added noble metals. The optimum operating temperatures range from 600 to 1200°F;

(b) Medium-temperature catalysts (Type B): The active components in this category are primarily base metals promoted with noble metals (other than ruthenium). The optimum operating temperatures range from 1000 to 1600°F; and

(c) High-temperature catalysts (Type C): In this group one finds single and multicomponent base metals on metallic or ceramic supports operating in a temperature range of 1200 to 1800°F.

In qualitative terms the performance of these three categories of catalysts may be summarized as follows:

Type A: The high activity of ruthenium-based catalysts with N_2 as the major product of NO_x conversion at moderate temperatures and rich carburetion offers considerable potential in terms of system design and location within the structure of the automobile. However, the problem of long-term stabilization of Ru-based catalysts to prevent metal loss with operating mileage has not been demonstrated.

Type B: The higher operating temperatures required by this type of base-metal/noble-metal catalyst combined with the tendency for ammonia production (as a by-product of NO_x reduction) present major hurdles to the utilization of this type of catalyst system.

Type C: Base metals on metallic supports have shown satisfactory performance at high temperatures (>1200°F). However, their susceptibility to deterioration under oxidizing/reducing (redox) cycling conditions requires further development and is at present limiting their utility.

The following sections will consider in more detail the makeup and basic performance characteristics of NO_x catalysts under controlled test conditions.

Catalyst details - Both monolithic and particulate (spherical or cylindrical) supports have found application in catalytic emission-control converters. Typical examples of the chemical composition of monolithic supports are given in Table 2.[2] The crystalline phase is made up of cordierite, with mullite and alpha-alumina as secondary phases. A suitable support material needs to withstand operating temperatures of 2200°F and exhibit high resistance to thermal shock and attrition.[3,4,5]

TABLE 2

Composition of Monolithic Catalysts Supports

	Percent Composition	
	American Lava	Corning
Major Components		
Cordierite ($2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$)	49-59%	86-98%
Alumina (Al_2O_3)	23-29%	3-5%
Mullite ($3Al_2O_3 \cdot 2SiO_2$)	14-18%	0.5-1.5%
Minor Components		
Iron (Fe)	0.5%	0.5%
Titanium (Ti)	0.4%	0.4%
Sodium (Na_2O) / Potassium (K_2O)	0.8%	0.2%

REF. 2

The ceramic support is provided with a "wash coat" which forms the high surface area substrate onto which the catalytically active metallic components are dispersed. Typically, the major component of the wash coat is gamma-alumina passed as a slurry of aluminum oxide monohydrate through the monolith to deposit a uniform film and subsequently calcined (heated) at high temperature.

By means of conventional wet-impregnation techniques, the noble metals are deposited on the wash coat. Generally, water-soluble noble-metal salts are employed at specified concentrations to yield the desired weight loading. The resulting material is air dried and reduced under specified conditions to yield highly dispersed metal crystallites. Typically, on a monolithic support the metal surface area is of the order of 0.5 m^2/g catalyst.

Ruthenium-containing catalysts need to be stabilized to prevent volatilization under oxidizing conditions due to the formation of volatile ruthenium oxides. To this end the addition of basic oxides,[6, 7

such as BaO, CaO, and La_2O_3, can result in formation of the thermally more stable ruthenate compounds. Preparation of stabilized Ru-based catalysts involves: (a) impregnation of the support material (either pelleted or monolithic) with a solution of the Ba-, Ca-, or La-salt; (b) calcination to form the corresponding oxide; (c) exposure to a solution of $RuCl_3$; (d) drying at 110°C; and (e) reduction in H_2 at 450°C. Alternatively, stabilized ruthenium catalysts have been prepared by applying to the ceramic substrate the Ba-, Ca-, or La-ruthenate compound as a suspension in the washcoat material.[7a]

Laboratory performance studies

Low-temperature catalysts - The activity pattern for NO reduction exhibits marked differences between some of the more active noble metals examined[6,8,9] as exemplified by the data in Figure 2 and Tables 3a and 3b. Although the results obtained under different experimental conditions of space velocity and gas composition point to some differences in the activity sequence, it becomes quite apparent that ruthenium occupies a unique position not only in terms of high conversion of NO but also in terms of relatively low production of ammonia as a by-product with nitrogen. This effect is demonstrated by the data presented in Figure 3 contrasting the behavior of alumina-supported Pt and Ru catalysts under similar experimental conditions.[10]

The decrease in ammonia formation exhibited by Ru catalysts is manifested also in bimetallic catalysts, such as Ru and Pd deposited on a ceramic support (see Table 4a).[3] It should be noted that the ammonia fraction in the product stream is significantly higher than would be expected for a Ru catalyst in the absence of added Pd. Also, the results indicate that addition of 1 vol% O_2 to the reactant stream causes a significant increase in NO conversion and a corresponding decrease in ammonia formation. However, the effect of oxygen appears to be deleterious to the long-term stability of the ruthenium catalyst, as demonstrated by the activity loss for NO conversion following exposure of the catalyst for 16 hours to 1 vol% O_2 at 1300°F.

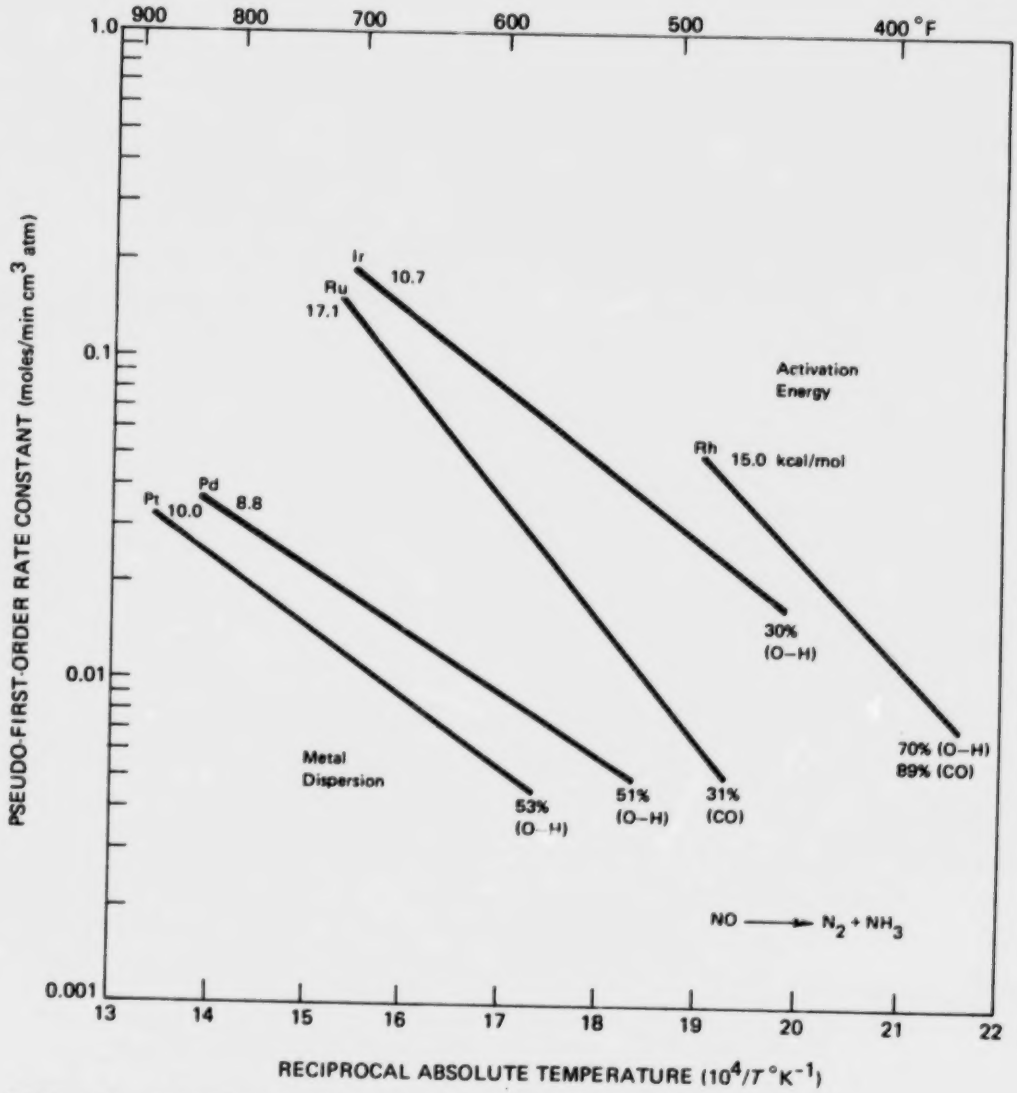

FIGURE 2 Relative Activity of Platinum Group Metals for NO Conversion. Nominal Loading, 1/8 in. Extrudates: 0.2 wt%: Activity: Rh > Ir > Ru >> Pd > Pt (per Atom Basis); Test Conditions: Synthetic Exhaust Gas with 45 ppm SO_2; GHSV = 138,000 hr^{-1}.

REF. 11

TABLE 3a

Performance of Supported Noble-Metal NO_x Catalysts

Catalyst	90% Convr. Temp., °F	NH_3 (PPM)	Selec. for N_2 (%)
0.37 wt% Ru/Al_2O_3	560	225	70
0.30 wt% Pt/Al_2O_3	700	650	13
0.30 wt% Pd/Al_2O_3	740	570	24

Feed stream: 0.1% NO, 1% CO, 0.3% H_2, 10% CO_2, 10% H_2O, balance N_2.

GHSV = 38,000 hr^{-1}; base was preformed Al_2O_3 Kaiser KC/SAF, surface area 260 m^2/g.
Surface area of ruthenium about 0.18 m^2/g catalyst.

REF. 8

TABLE 3b

Performance of Supported Noble-Metal NO_x Catalysts

Catalyst	90% Convr. Temp., °F	Selectivity for N_2, (%)
0.5 wt% Ru/Al_2O_3	380	92
0.5 wt% Rh/Al_2O_3	495	66
0.5 wt% Pd/Al_2O_3	590	25
0.5 wt% Pt/Al_2O_3	750	22

Feed stream: 0.5% NO, 2% H_2, 2% CO, balance He

GHSV: 24,000 hr^{-1}

REF. 6

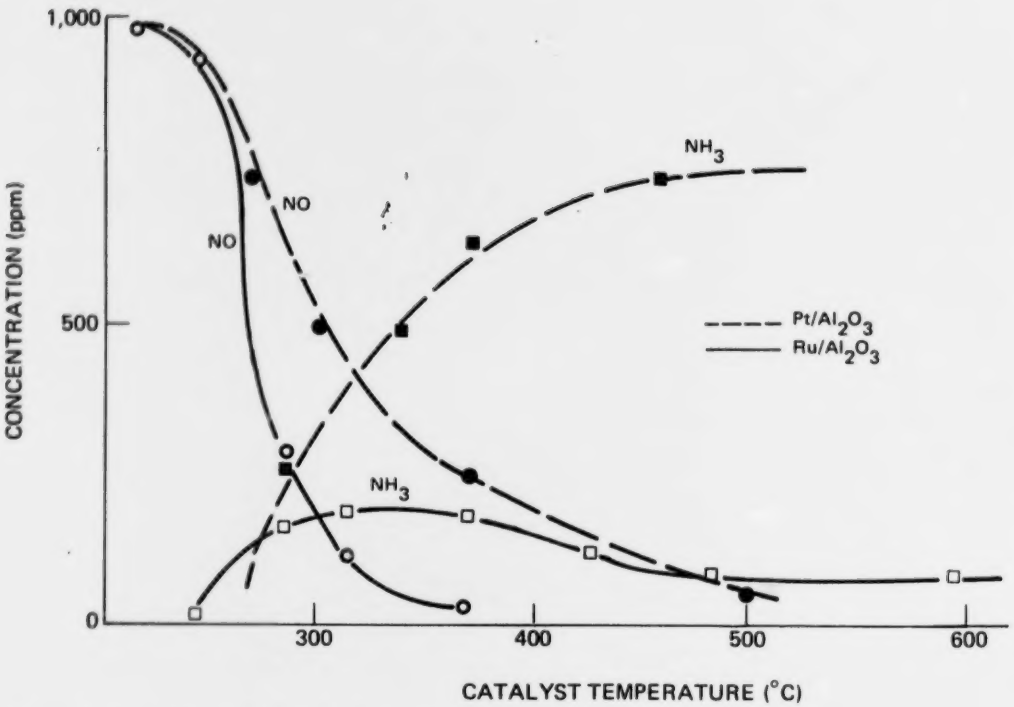

FIGURE 3 Comparison of Ammonia-Forming Tendencies and NO Reduction of Supported Pt and Ru NO_x Catalysts. Feedstream: 0.1% NO, 1.0% CO, 10% CO_2, and 10% H_2O in a N_2 Atmosphere; GHSV = 38,000 hr^{-1}.

REF. 10

TABLE 4a

Performance of Supported Mixed Ru/Pd NO_x Catalysts

Pretreatment	Gas Composition	90% Convr. Temp., °F	Max. % N_2 Selectivity
1500°F (N_2)	a	520	65
1500°F (N_2)	a + 1% O_2	450	90
1300°F (1% O_2 for 16 hrs)	a	670	80
1300°F (1% O_2 for 16 hrs)	a + 1% O_2	530	90

Noble-metal loading: 0.2 wt% each metal

Gas Composition a: 2000 ppm NO, 200 ppm HC, 2% CO, 3% H_2O, balance N_2

REF. 3

Apparently due to the formation of volatile ruthenium oxides (RuO_3 and RuO_4 see Table 5),[6] loss of the active Ru component occurs with simultaneous enhancement in ammonia formation. An effort has been made to stabilize ruthenium (or its oxide) by adding a foreign basic oxide (e.g., BaO, CaO, or La_2O_3) to form thermally more stable crystal phases such as the perovskite structure of $LaRuO_3$.[6,7,7a] The degree of stabilization can be seen from the data in Table 6.[7] At temperatures in excess of 1000°C, $BaRuO_3$ converts into BaO and Ru under reducing conditions, but it can be partially reformed under oxidizing conditions.[7] A more oxidation-resistant catalyst, designated X-22, has now been reported by Kobylinski and co-workers.[7a]

Flow-reactor studies employing monolithic and pelleted catalysts (Tables 7 and 8) and synthetic gas mixtures have indicated that the addition of the foreign oxides impairs neither the N_2 selectivity nor the conversion activity of the catalysts. Similar

TABLE 5

Volatilities of RuO_3-RuO_4

Temp. (°F)	% O_2	ppm RuO_x*
900	2	0.005
900	5	0.01
1000	2	0.01
1600	2	2.83
1600	5	5.31
1800	2	19.41
2000	2	79.83
2000	5	130.41

*Concentration in static system at equilibrium vapor pressure, calculated.

Comparison of Stability of Bulk RuO_x and "Stabilized" $BaRuO_3$ Supported and Unsupported Catalysts

	RuO_x		$BaRuO_3$	
T (°F)	Bulk	Supported	Bulk	Supported
1000	0	0	0	0
1400	14	22	0	1
1600	40	62	2	18
1800	85	100	16	58

(The numbers are weight % loss of Ru metal after treatment in flowing 4% O_2 - 96% He for 8 hours)

REF. 6

TABLE 6

Comparison of Ruthenium Loss in a Ruthenium Catalyst and in Barium Oxide- or Lanthanum Oxide-stabilized Ruthenium Catalysts

Temperature		Exposure Time in Hours	Ruthenium Loss percent		
°F	°C		Ru Catalyst	Ru-BaO Catalyst	Ru-La_2O_3 Catalyst
950	510	16	0	0	0
1350	730	4	13	0	0
1450	785	4	45	0	0
1530	830	4	90	25	5
1630	885	4	--	25	25
1750	955	4	--	--	25
1820	995	4	--	75	--

Conditions:
- Space velocity : 38,000/h
- O_2 concentration in nitrogen: 2.5-3 percent
- Ru content : 2000 p.p.m.
- La or Ba (as metal) content : 3 percent by weight
- Support : UOP Al_2O_3 pellets

REF. 7

TABLE 7

Performance of a Presynthesized $BaRuO_3$ Monolithic Catalyst

Temperature °C	$NO-H_2$ System		$NO-H_2-CO$ System		$NO-CO-H_2O$ System	
	% NO Converted	p.p.m. NH_3 Formed	% NO Converted	p.p.m. NH_3 Formed	%NO Converted	p.p.m. NH_3 Formed
202	23.9	18.9	56.8	60.5	N.M.	N.M.
255	89.6	75.0	100	212	N.M.	N.M.
278	100	92.4	100	228	100	380
320	100	186	100	233	100	310
360	100	190	100	263	100	260
447	100	63.2	100	251	100	175

Conditions: Space velocity : 20,000/h
Inlet NO concentration: 100 p.p.m.
Inlet CO concentration: 1.5 percent
Inlet H_2 concentration: 1.43 percent
Inlet H_2O concentration: 10 percent
Catalyst support : Corning monolith

N.M. = not measured

REF. 7

TABLE 8

Comparison of Activity and Selectivity between Stabilized and Non-stabilized Ruthenium Catalysts. System $NO-CO-H_2$

Temperature °C	Ru Catalyst		Ru-BaO Catalyst		$Ru-La_2O_3$ Catalyst	
	% NO Converted	p.p.m. NH_3 Formed	% NO Converted	p.p.m. NH_3 Formed	% NO Converted	p.p.m. NH_3 Formed
250	85	45	35	30	80	55
300	100	85	92.5	80	98	150
350	100	118	100	135	100	210
400	100	135	100	210	100	208
450	100	137	100	250	100	190
500	100	---	100	220	100	50

Conditions: Space velocity 20,000/h
Inlet NO concentration : 1000 p.p.m.
Inlet CO concentration : 1.5 percent
Inlet H_2 concentration : 1.43 percent
Catalyst support : low-shrinkage American Cyanamid alumina pellets
Ru content : 2000 p.p.m.
La or Ba (as metal) : 3 percent by weight

REF. 7

conclusions have been reached by others,[12] although at least one company reported that complete stabilization of the ruthenium resulted in an inactive catalyst.[13] Since the NO_x-reduction catalysts are designed to operate in an overall-reducing atmosphere on the automobile, deterioration of the mixed-oxide ruthenates remains a serious problem especially under cyclic redox operation. It is to be expected that the reduction to metallic Ru in admixture with the basic oxides will ultimately cause the formation of Ru metal crystallites that will tend tc volatilize on oxidation. Thus, even the stabilized ruthenium catalysts (Table 4b)[11] demonstrate loss in conversion efficiency due to exposure to oxidizing and reducing conditions. In reference 14, the following conclusions are reached concerning the ruthenium catalysts:

> At this intermediate stage in our work, it looks as if at least some stabilized ruthenium NO_x catalysts might be viable under normal, average driving conditions. Further improvement is necessary, however, to permit ruthenium to be used under the more severe conditions which can be encountered, perhaps even routinely, in actual automobile operation.

TABLE 4b

Effect of Redox Cycling on Performance of Stabilized NO_x Catalyst

	90% Convr. Temp., °F	
Catalyst	Fresh	After Cycling
A	625	700
B	625	>1100

Cycling: Alternating oxidation-reduction atmospheres for 64 hours at 1200°F

REF. 11

Medium-temperature catalysts - Typical catalysts in this category are the supported base metals with and without noble-metal additives.[8,15] Their performance on exposure to a synthetic gas mixture is exemplified by the data in Table 9.[15] The Cu-Ni system (on a monolith support), the Pt-Ni system (on a pelletized support) are highly active for NO_x conversion, and the reduction of NO_x is accompanied by appreciable NH_3 formation.

To elucidate in more detail the performance characteristics of the Ni-Pt (Ni/Pt = 500/1) catalyst on a monolithic support, laboratory tests were performed in which the CO/O_2 ratio of the reactant gas mixture and the temperature were varied over a wide range.[11] The results of these tests demonstrated that for $CO/O_2 < 1.5$ (net oxidizing) the activity for NO_x conversion rapidly decreased. In contrast, the nitrogen selectivity diminished with increasing CO/O_2 exhaust gas ratio, especially at temperatures below 1100°F (see Figure 4).[11] Thus, for net NO_x conversion efficiency >80%, the operation of this catalyst required gas mixture compositions with a CO/O_2 ratio between 1.5 and 3.0 (A/F = 14.65 to 13.5). In comparing the N_2 selectivity of the Ni-Cu and Ni-Pt catalysts with that of ruthenium as a function of the CO/O_2 ratio, one observes marked differences between base- and noble-metal additions to the Ni catalysts (Figure 5).[11]

High-temperature catalysts - The development of an all-metal catalyst system (support and substrate) for NO_x reduction offers several potential benefits--for example: (a) a low-pressure drop across the open mesh metal/support configuration: (b) a low-mass and relatively low-heat capacity metallic construction: and (c) a high specific surface area of active catalyst. Of numerous non-noble metal elements studied for NO_x conversion,[3] the systems based on Ni and Cu appear to offer some promise for further development. Foremost in this area have been the GEM catalysts in which Ni-Cu alloys[16] represent the catalytically active component deposited on high-temperature corrosion-resistant metallic support. In laboratory tests[17] with synthetic reactant gas mixtures, this catalytic system exhibited

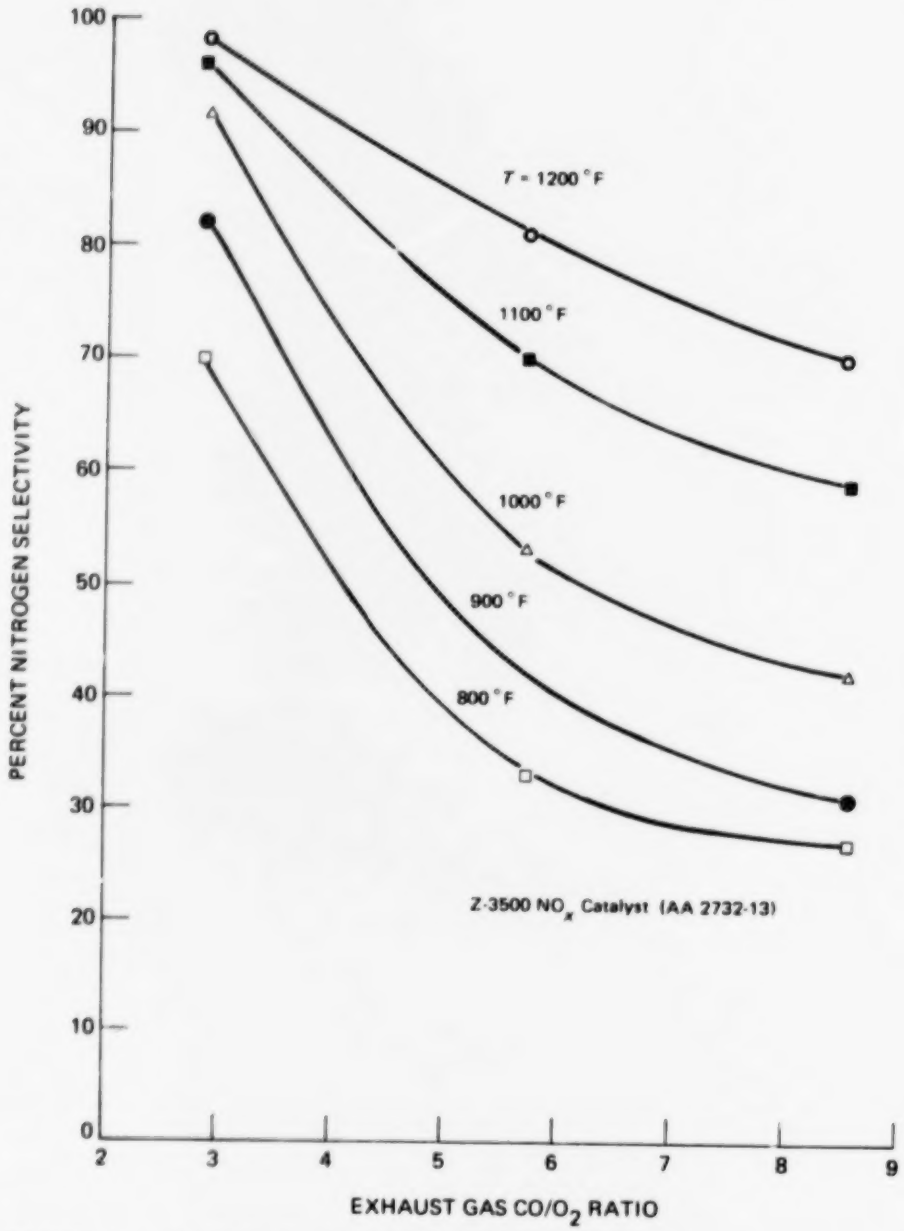

FIGURE 4 Selectivity for N_2 of a Ni/Pt NO_x Catalyst versus CO/O_2 Ratios. Bench Unit Data: Synthetic Exhaust Gas, 45 ppm SO_2; GHSV = 138,000 hr^{-1}.

REF. 11

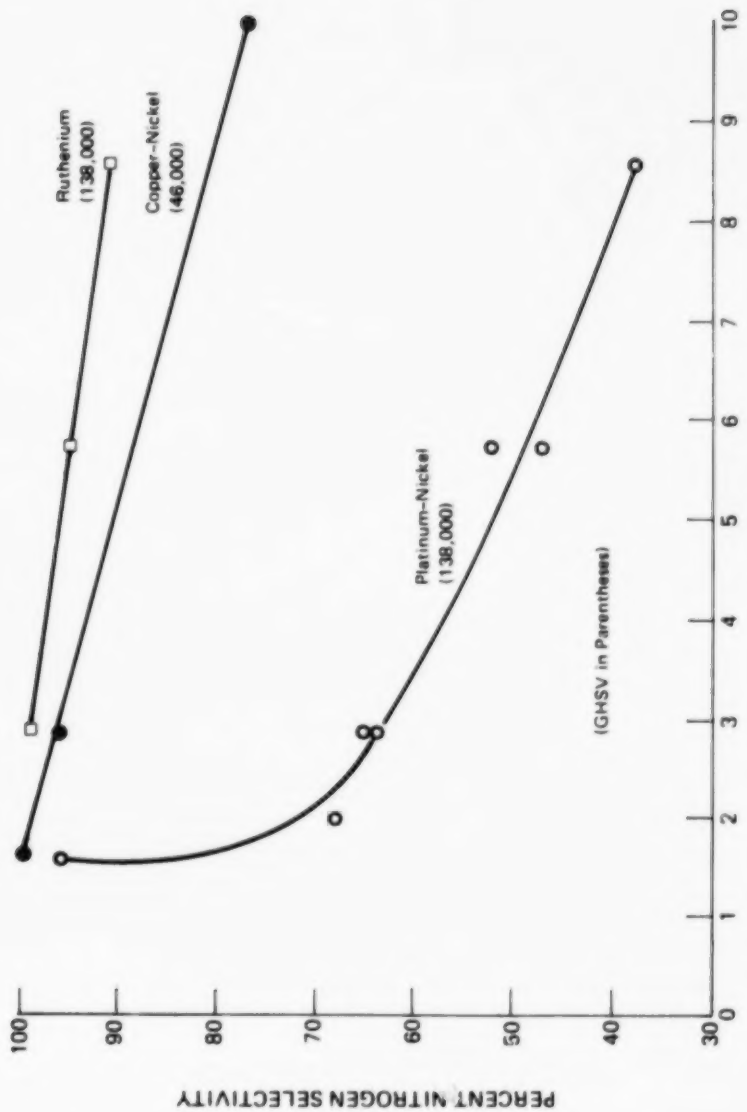

FIGURE 5 Dependence of N_2 Selectivity on CO/O_2 Ratio. Test Conditions: Synthetic Exhaust Gas, 45 ppm SO_2; Temperature: 1000°F; 1/8 in. Extrudates.

REF. 11

TABLE 9

Performance Data for Base-Metal and Promoted Base-Metal NO_x Catalysts

Catalyst	% NO_x Conversion	% N_2 Selectivity
Ni-Cu (monolith)	100	72
Ni-Pt (extrudate)	99	59

Gas Mixture: 1.0% CO, 0.33% H_2, 0.35% O_2, 0.08% NO, 0.10% C_3H_8, 10% H_2O, 13% CO_2, balance N_2.

Conditions: GHSV = 45,000 hr^{-1}; Exit bed temp. = 1000°F.

Conversion: Fraction NO_x converted to products.

Selectivity: Ratio of volume fraction N_2 formed to NO_x converted.

REF. 15

the performance data shown in Figure 6a. Net NO_x conversion in excess of 75 vol% has been obtained at residence times of just over 15 milliseconds.

As reported earlier,[18] the NO_x conversion is accompanied by ammonia formation (especially at temperatures below 1200°F). Its concentration goes through a maximum with increasing residence time in the catalytic reactor. In the presence of oxygen (Figure 6b), the formation of ammonia is greatly suppressed. However, it has already been noted that the presence of oxygen at a level of 1 vol% retards the conversion of NO_x. This observation is further amplified by the results derived from experimental studies of the effect of O_2 on the NO reduction rate (Figure 7).[17] A sharp decrease in rate is recorded as the oxygen level approaches 1 vol% in the gas stream. These data suggest that at sufficiently high concentrations the oxygen preferentially occupies the surface sites required for dissociative NO sorption on the catalyst surface.[16]

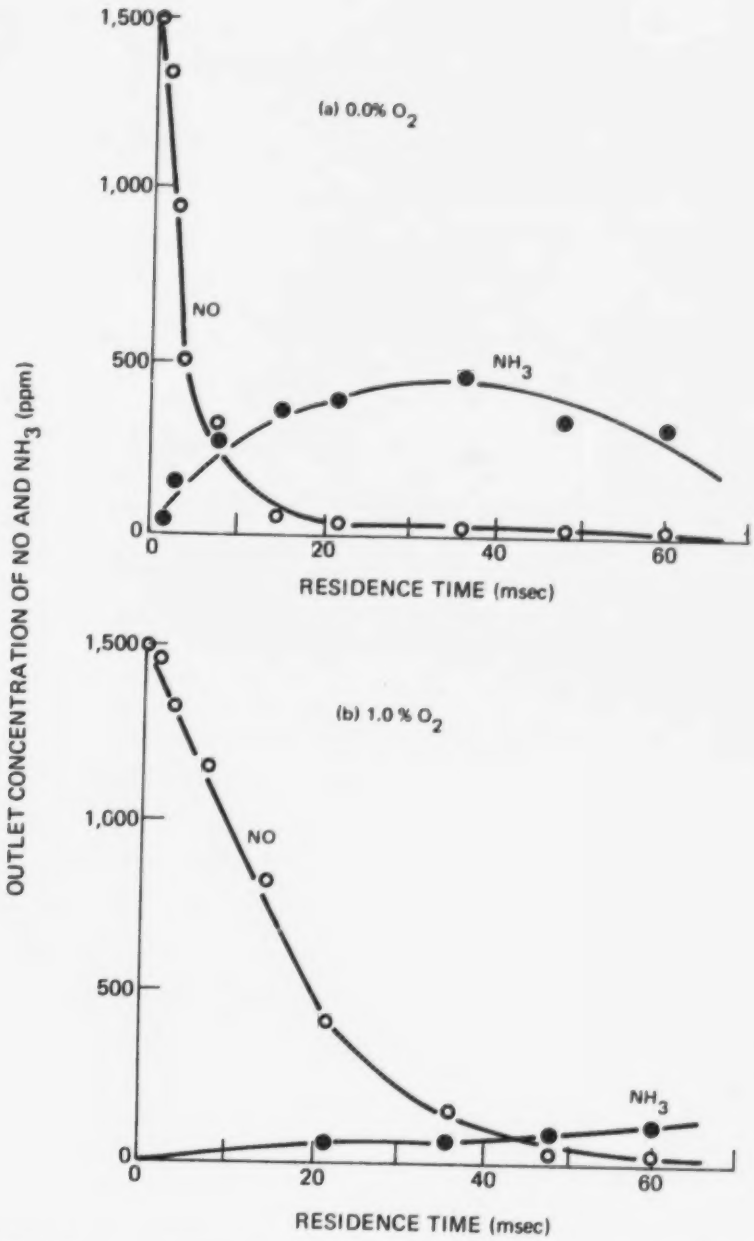

FIGURE 6 Dependence of NO Reduction and NH_3 Formation on Residence Time Evaluated for GEM Catalyst at 1200°F and 10^5 hr^{-1}. Feed Gas: 1,500 ppm NO, 500 ppm HC, 1.5% CO, 0.5% H_2, 12% CO_2, 10% H_2O, O_2 as Indicated, and Balance N_2.

REF. 17

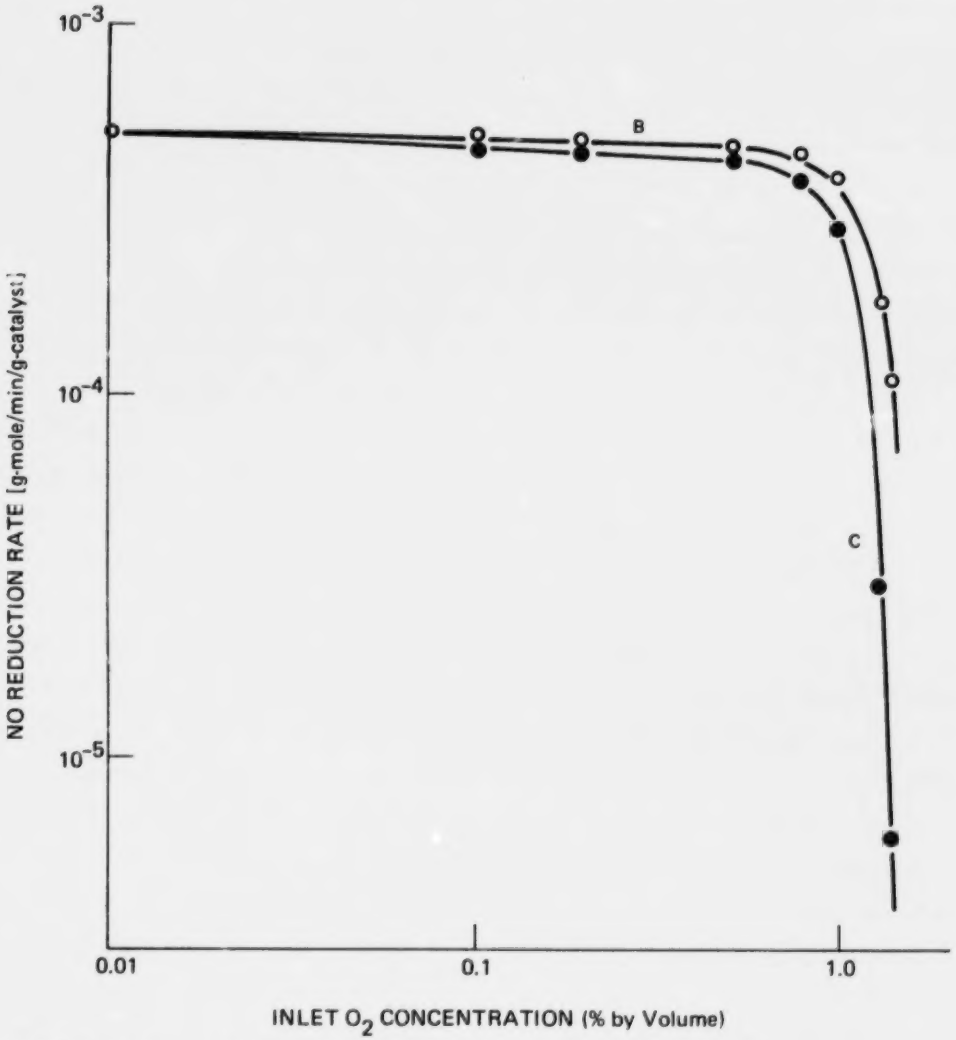

FIGURE 7 Dependence of NO Reduction Rate on Inlet O_2 Concentration. Curve B - Short Exposure to O_2, Curve C - Long Exposure to O_2. Feed Gas: 1.5% CO, 12% CO_2, 10% H_2O, 500 ppm HC, 1,500 ppm NO, and Balance N_2. Temperature: 1200°F; Space Velocity: 6×10^5 hr^{-1}.

REF. 17

In order to decrease the ammonia-forming tendencies, a modified Ni-Cu catalyst was developed[19] containing Ni, Cu, Cr, and Co; this catalyst is known as GEM-68. Its performance characteristics under laboratory conditions are shown in Figure 8. It is apparent that the total and net NO conversion efficiencies of this material are superior to those of its predecessors (e.g., GEM-67, etc.). Furthermore, it is a low-ammonia former even in the absence of gaseous O_2.

Of critical concern to the applicability of the metal-catalyst system is its susceptibility to deterioration and mass loss in the presence of excess oxygen. An interesting approach to the solution of this problem involves the GEM-68 catalyst in combination with an "oxygen getter" placed on the upstream side of the NO_x-reduction catalyst. In one of the configurations, the "getter" contains a noble-metal catalyst that effectively removes oxygen by catalytic reaction with the various reducing agents present in the fuel-rich reactant gas mixture, e.g., H_2, CO, and HC. By close control of the space velocity, such a system yields high NO_x-conversion efficiency and low ammonia formation under the selected laboratory conditions (Figure 9).[19]

For vehicle application, the laboratory results suggest the following requirements for this all-metal catalyst system: (a) net fuel-rich exhaust gas mixture with CO/O_2 ratios greater than 1.5: (b) exhaust bed temperatures near 1200°F (temperature limit 1600-1800°F): and (c) space velocities of the order of 10^5 hr^{-1}. In vehicle tests the light-off temperature of GEM catalysts has been found to be between 850 and 900°F, a temperature range that exceeds by 200-250°F the temperature attained by the catalyst bed during the inital 20 seconds of the FTP cycle.

Similarly, in the "Reverter Emission Control System,"[20] the use of an all-metal catalytic device has been adopted. The "Reverter" system includes three stages, only one of which involves a catalytic process (the second). In this second stage, a base-metal catalyst on a metallic grid reduces NO_x to N_2 by reaction with CO, HC, and/or H_2 in the exhaust system.

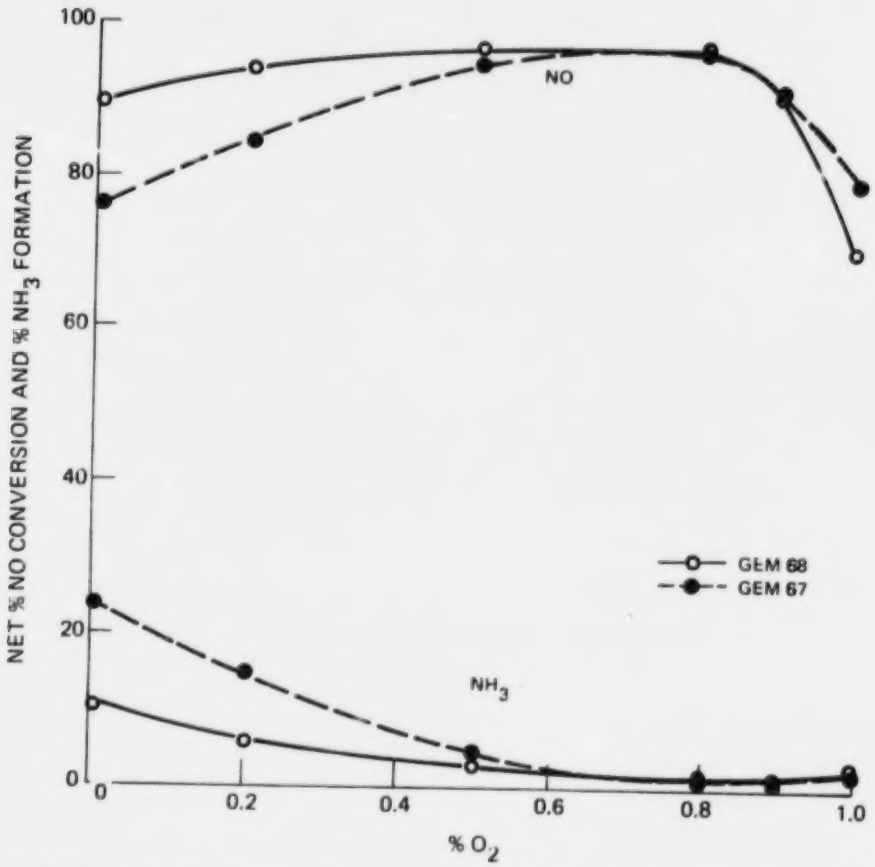

FIGURE 8 Comparison of Ammonia Formation on GEM-67 and GEM-68 as a Function of O_2 Concentration. Feed Gas: 1,500 ppm NO, 500 ppm HC, 1.5% CO, 12% CO_2, 0.5% H_2, 10% H_2O, Balance N_2; Space Velocity: 10^5 hr^{-1}.

REF. 19

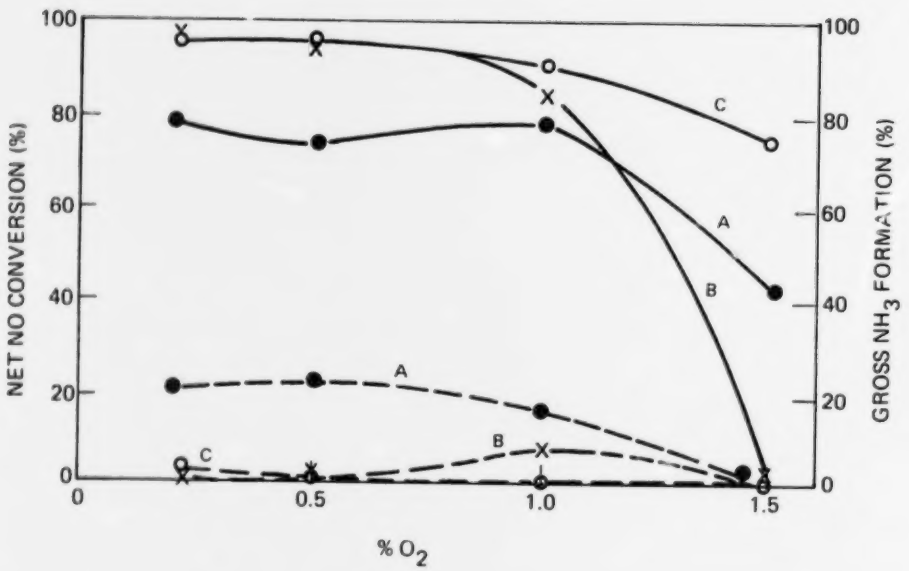

FIGURE 9 Performance of GEM-68 "Getter" System. Curves A and B: Previous Data; Curve C: GEM-68 System with Upstream PTX-A "Getter." Temperature of NO_x Catalyst: 1200°F; Space Velocity: 10^5 hr^{-1}.

REF. 19

A number of high-temperature, base-metal alloys were examined for their activity as exhaust-control catalysts and their corrosion resistance under redox conditions. The type of catalytic materials examined and their relative reactivities are shown in Figure 10.[20] None of these have withstood the rigors of long-duration vehicle tests. Most recent tests have involved a three-component metal composition (Cu-Cr-Ni) applied to an expanded-metal substrate of Inconel-601 alloy. At $CO/O_2 < 0.1$ and operating temperatures of 1500-1800°F, this system exhibited more than 90% (gross) NO_x conversion. The fractional conversion to NH_3 was not given,[21] although it was probably quite low at these temperatures. One strong point favoring this high-temperature system is insensitivity to lead.

Ammonia-oxidation catalysts ("three-bed" system) - A problem common to the NO_x catalysts discussed in the preceding sections is the tendency to form ammonia. It appears that this by-product, in the presence of excess oxygen, is rapidly reoxidized to NO_x in a dual-catalyst system (a tandem arrangement in which a NO_x reduction reactor is followed by an HC and CO oxidizing reactor). As a result, the concept of a triple-bed catalyst has emerged[2,13] which incorporates three catalytic reactors in series (one for NO_x reduction, one for NH_3 oxidation, and one for HC/CO oxidation). The system provides for the controlled introduction of air to the NH_3 catalyst section for oxidation to nitrogen before coming in contact with the oxidation catalyst for HC and CO. Such a scheme would greatly relax the limitations imposed on a number of available NO_x catalysts that exhibit high activity for gross NO_x but too much ammonia formation. At the same time, the three-bed system adds some complexity due to increased catalyst mass, warm-up time, and engineering design. As of the time of this writing, the selection of a suitable ammonia-oxidation catalyst has not taken place. The scientific literature[22,23] suggests that some base-metal oxides exhibit the needed high N_2 selectivity for ammonia oxidation. At the same time, such catalysts tend to oxidize hydrocarbons incompletely (oxidative dehydrogenation to olefins and partial oxidation to aldehydes, ketones, etc.), so that the third catalytic section would still be required to convert these intermediate products into CO_2 and H_2O. The development of the three-bed catalytic system represents an interesting approach to the NO_x

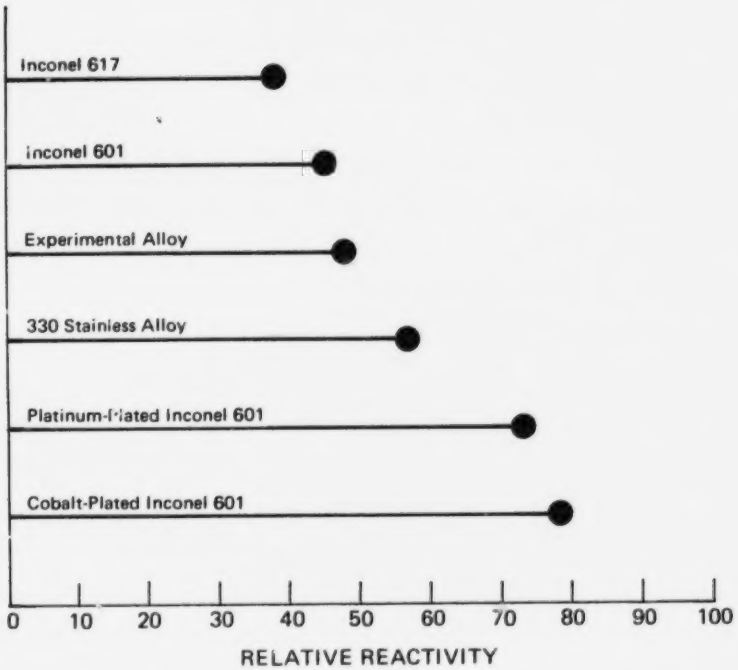

FIGURE 10 Relative Reactivity of Catalysts in Questor's Reverter.

REF. 20

conversion problem which, in spite of added complexity, may offer some promise of meeting the ultimate NO_x standards of 0.4 g/mi, at least at low mileage.

C. Three-Way Catalytic Systems

In the dual-bed and triple-bed catalytic systems, both oxidizing and reducing conditions are simultaneously required in separate reactors to effect decomposition of all three pollutants. It is possible, however, to convert the three pollutants in a single reactor if just the right set of conditions can be maintained. While NO_x removal requires net reducing conditions and HC and CO require oxidizing conditions, all three pollutants can be converted simultaneously at A/F ratios at or slightly lean of stoichiometic as illustrated in Figure 11.[24] Unfortunately, with most catalysts this "window" for effective performance is exceedingly narrow, being the order of $\pm$0.1 A/F ratio units. Such control is impossible with present carburetors alone because of the variation in the mixture with vehicle operating mode. About the only way to obtain such precision is through the use of an oxygen sensor coupled with a feedback loop to control the A/F ratio. Intensive work is in progress in the U.S., and particularly in foreign countries (e.g., Germany), to develop such a system that will withstand the thermal cycling, poisoning effects, and vibration that would be present in automobile exhaust systems. To minimize instabilities in the feedback circuit, some manufacturers[25] have suggested using more than one sensor at different points in the exhaust system. Such an approach offers several advantages since it involves only one catalyst bed and requires operation at a point where neither automobile performance nor fuel economy will be impaired.

Neither the catalysts nor the sensors for such a system have been perfected. Work is continuing on the development of catalysts with wider windows which will decrease the degree of carburetion control required. Most catalysts presently being investigated contain

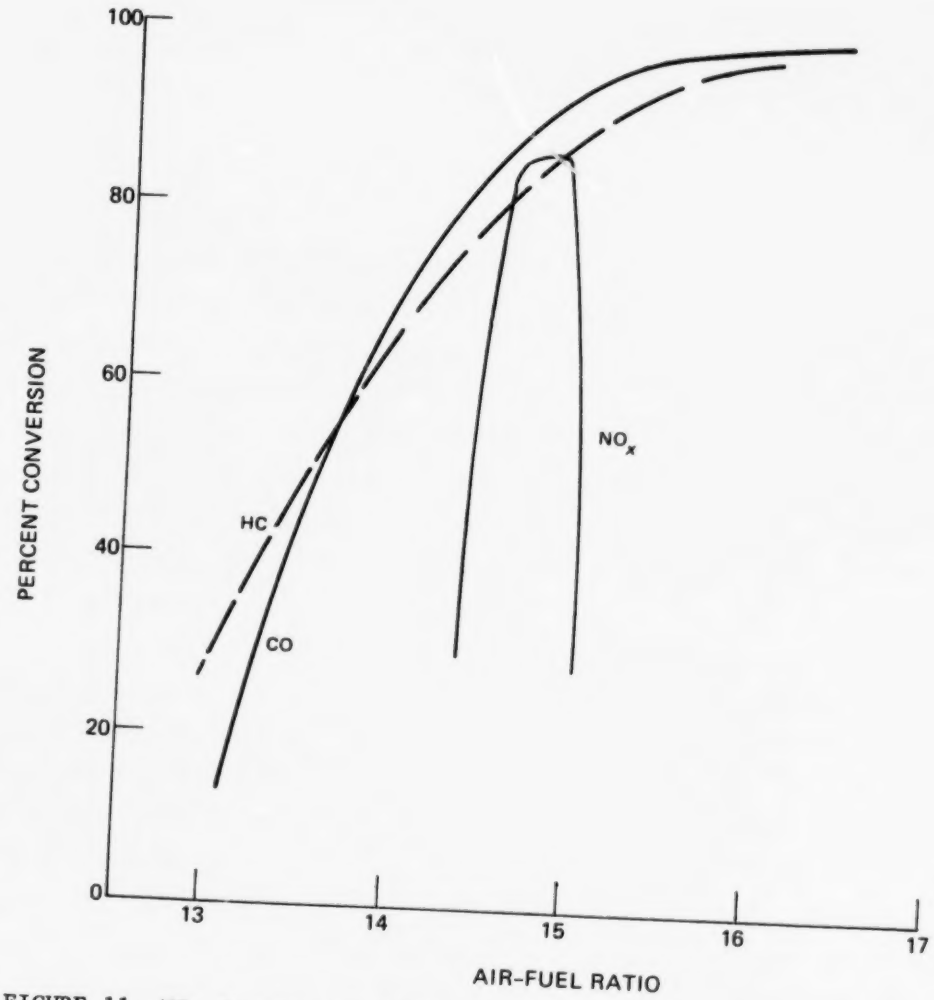

FIGURE 11 NO_x Conversion Window for Three-Way Catalyst.
REF. 24

noble metals, specifically Pt, Pd, Rh,[2] (and possibly Ru). Not only does the catalytic activity decrease with age, but the "window" has been observed to shift slightly for some catalysts, as will be discussed in detail in the next chapter. Also, the sensor response does not remain exactly constant as it ages, and these two changes could be sufficient to make the system completely ineffective for one group of pollutants after it had aged, even though it was perfectly calibrated when new.

D. Discussion

The laboratory studies offer a valuable guide to the evaluation of NO_x catalysts for application to automobile exhaust control. A number of parameters need to be considered, some of them exhibiting supporting, others, opposing effects as shown by the data entered in Table 10. The choice of N_2-selectivity as the important criterion for catalyst selection will lead to an entirely different system than the criterion of minimum temperature required for 90% NO_x conversion (activity). At the same time, it is to be recognized that the feasibility of a three-bed catalyst system ((1) NO_x reduction, (2) NH_3 oxidation, (3) HC/CO oxidation) makes the low-temperature, noble-metal catalysts contenders for NO_x removal. Similarly, the high-temperature, all-metal catalyst systems become interesting by going to a three-bed catalyst system ((1) O_2 removal, (2) NO_x reduction, (3) HC/CO oxidation). The catalyst technology available at this time offers no other alternatives in meeting the standards of 0.4 NO_x g/mi. It is somewhat surprising that the development effort in the use of three-bed catalytic systems has not advanced sufficiently to evaluate in some detail the potential utility of such systems in vehicle operations.

While the laboratory tests have served as guides to the development of new systems, the ultimate test is performance in automobiles operated under realistic conditions, which is the topic considered in the next chapter.

TABLE 10

NO_x Catalyst Performance Summary
(Qualitative)

System	NO_x Activity T 90% Convr.	Redox Stability	N_2 Selectivity	Range[a] CO/O_2	Poisoning[b] Resistance	Durability
Supported noble metal (not Ru)	600-1200°F	A	C	3	C	A
Supported, stabilized Ru	1000°F	B	A	3	B	C
Supported base metal	1000-1600°F	B	B	2-3	B	B
All metal	1200-1800°F	C	A	10	A	B

A = high; B = moderate; C = poor

a - CO/O_2 ratio is representative of air/fuel ratio (when allowance is made for hydrocarbons typically present in the exhaust, a ratio of <1.5 indicates net oxidizing condition)

b - Poisoning resistance to Pb, P, S

IV. VEHICLE PERFORMANCE AND DURABILITY OF AUTO CATALYSTS

In an earlier report,[26] the overall deterioration of automobile-exhaust, emission-control catalysts was separated into two components: deterioration due to deactivation and deterioration due to poisoning. The same breakdown will be used in this chapter. The first category would include those factors encountered in operation with contaminant-free fuel and oil and represents deterioration due primarily to alteration of the physical nature of the catalyst. The second includes factors encountered upon contamination of the active-catalyst surface and represents deterioration due primarily to alteration of the chemical nature of the catalyst.

In this chapter the durability discussion sequence will begin with oxidation catalysts and then proceed to various HC/CO/NO_x systems. Although a complete division between deactivation and poisioning effects is not possible, one may generally associate slow, long-term decreases in activity to deactivation and initial rapid losses in activity to poisoning.[26,27] While a reasonably comprehensive picture of both deactivation and poisoning is now available for oxidation catalysts alone, there is as yet very little information regarding the long-term durability of catalytic systems for NO_x control.

No attempt will be made to discuss all catalysts here, only those which, in the case of oxidation, have been developed to the point of application or, in the case of NO_x, are the most promising candidates. By and large, these are all noble-metal formulations, except for the high-temperature systems discussed in the preceding chapter.

A. Deactivation of Oxidation Catalysts

The primary mechanism for deactivation is the sintering or agglomeration of the small crystallites of active metallic components by a thermal mechanism. Associated with sintering of the supported metal may also be deterioration of the support structure and changes in the

nature of the support-catalyst interaction. All these processes are characterized by high activation energies; they occur to only a minimal extent at normal temperatures of operation (900-1200°F). Thus, the extent of deactivation is primarily a function of the prior thermal history of the catalyst.

The most severe mode of deactivation is, of course, melting. For pelleted catalysts that use gamma-alumina, melting temperatures are around 3700°F; this failure mode is not important.[25] However, changes in pore-size distribution and decreases in the pellet volume can occur at substantially lower temperatures. Monoliths, melting in the range of 2400-2500°F, have more of a problem, although some monoliths are now claimed to be stable to 2800°F.[28] The specific conditions associated with melting are: (1) dieseling after ignition shutoff; (2) running out of fuel; (3) long downhill deceleration; and (4) ignition failure. In each case the ultimate effects depend on the frequency of such incidents. In sintering, as opposed to melting, occasional temperature excursions in the range of 2000°F can be tolerated by existing monoliths containing noble metals; fouling of one or even two plugs can be withstood under normal (50-mph, steady-state) conditions.[2] Melting of monolithic supports due to abnormal driving modes is apprently more frequent with small displacement engines (e.g., 4-cylinder) than with larger vehicles.[29,30] One manufacturer of small displacement automobiles[30] felt that the incidence of failure due to overheating from abnormal driving modes could be as high as 25% over 50,000 miles. With manual choke on after a cold start, they have measured converter temperatures as high as 2400°F on downhill deceleration.

Conditions that result in over-temperature failures of various ceramic monolithic oxidation catalysts apparently will be almost eliminated by engine modifications (such as solid-state ignition, higher voltage, and longer spark). Exxon[31] indicated that the catalysts indeed serve as an unintentioned but highly sensitive detector of

ignition malfunction; Engelhard reinforced this belief claiming that the automobile manufacturers have told them not to be concerned any longer about over-temperature as a significant problem because of basic engine improvements.

Catalyst attrition, potentially leading to enhanced particulate emissions, was not reported as a problem in a single visit to catalyst or automobile manfacturers. Corning claims to have eliminated wash coat peeling about two years ago by development of monoliths with pore sizes several times that of alumina particles in the adhering wash coat.[28] The Rhone-Progil alumina pellet, as well as the W.R. Grace manufactured extrudate formulation, have led to pellet oxidation catalysts meeting General Motors' constraints for particulates.[25] Remaining attrition problems now appear associated largely with loading techniques for "canning" the monolith or pellets and with quality control for the large-scale manufacture of these materials,[28,32] although Houdry is still searching to develop a better pellet support than the imported Rhone-Progil candidate. Health hazards that may be associated with attrition are discussed in the next chapter.

These findings underscore a basic mood shift from two years ago. The successful catalyst competitors appear to have most of their manpower now on quality control problems and manufacturing debugging for oxidation-catalyst production. Efforts in new catalyst development have almost ceased.

B. Deactivation of NO_x Catalysts

At the present state of the art, the various NO_x systems are more susceptible to thermal damage than oxidation catalysts alone. All automobile and catalyst manufacturers visited voiced this opinion. The NO_x systems developed by Questor and Gould seem particularly susceptible to thermal damage, oxidation and loss of particulate oxide matter in the former case,[21] melting in the latter.[19] Both of these manufacturers have developed improved systems to avoid such thermal damage, which is associated with oxidizing conditions. Questor has a

pre- and post-bed air-injection system that is designed to keep inlet O_2/CO ratios in the range of 0.004-0.4 while maintaining the catalyst (Cu-Cr-Ni alloy, IN-1013, bonded to Inconel 601) operating temperature from 1500-1800°F, which can be tolerated. Gould has incorporated a monolithic oxidation catalyst in the system upstream of their NO_x catalyst (Cu-Ni-Co-Cr on a high Ni-alloy base) to remove O_2 from the exhaust mixture, as discussed in the preceding chapter.

Thermal degradation of Ru-based NO_x catalysts is associated with oxidation-reduction cycling. This involves a gradual separation and agglomeration of Ru metal from the stabilizing structure whereupon it is oxidized to volatile ruthenium oxides,[33] as discussed in chapters III and VI. The net rate of volatilization is probably thermally controlled due to the high activation energy for Ru metal diffusion in the catalyst matrix. Volatilization of current supported Ru formulations (primarily based on $BaRuO_3$) becomes a problem at temperatures above 1100-1200°F, although the exact temperature range where trouble begins depends on the severity and frequency of redox cycling. Normal operating temperatures for NO_x systems may vary from 900-1500°F for large engines, 1100-1700°F for small engines.[32] Some representative data on temperature excursions in NO_x portions of a two-bed system from abnormal driving modes in small displacement autos are given in Table 11.[29]

Noble metal-base metal combinations are of interest to some manufacturers because of their improved thermal stability. These are normally mixtures containing Ni and Rh (and in some cases Pt and/or Pd), and these can be stabilized to have thermal durability comparable to current oxidation catalysts.

Another form of deactivation appears in the Gould GEM system. This is called "green rot,"[19] which is a term describing the flaking off of the thick active ingredient layer from the base metal. This embrittlement process arises from attack at the grain boundary of the support and is associated with oxidation/reduction cycling which the improved GEM-68 system avoids (see preceding chapter).

TABLE 11

Abnormal Driving Modes - Effect of Misfiring Cylinder

Datsun P610 mounted on Chassis Dynamometer
Exhaust Manifold-Mounted NO_x Catalyst System

Rise of NO_x Catalyst Bed Temperature, ^oF

Vehicle Speed (km/hr)	Bed Temperature	
	Normal Opn.	1 Cyl. Misfiring
60	1060	→ 1640 (after 80 secs)
80	1240	→ 1740 (after 50 secs)
100	1330	→ 1740 (after 33 secs)

REF. 29

C. Deactivation of Three-Way Catalysts

To date there have been few data presented concerning the deactivation of three-way $HC/CO/NO_x$ catalysts. However, the composition of most of these catalysts appears to be a variation on current oxidation catalysts, involving Pt, Pd, Rh, or combinations thereof. Thus, it would seem reasonable to assume these three-way systems will have thermal durability comparable to the existing oxidation catalysts. As important as the thermal stability of the catalysts is the stability (and thermal response) of the oxygen sensor used with three-way catalysts. Most sensors that are currently under evaluation or testing are based on zirconia. The normal configuration employs a doped zirconia thimble with platinum electrodes mounted on a device which looks very much like a spark plug. There have been some instances of sensor failure due to thermal shock, but this seems a minor factor in the determination of their durability. Poisoning is the problem here, as will be discussed subsequently.

D. Poisoning of Oxidation Catalysts

Catalyst poisoning, in the automobile emission context, is largely chemical in nature, although physical factors can in some cases be important. An empirical approach to the catalyst-poisoning field appears most sensible here. In the context of the charge to the Panel of Consultants on Catalysts, that of assessing the feasibility of catalyst usage on vehicles, the order of decreasing utility of catalyst poisoning studies is apparently: (1) vehicle data; (2) multicylinder engine data, preferably over a realistic driving cycle rather than at steady state; (3) single cylinder data; and, finally, (4) bench-scale synthetic atmosphere tests with potential catalyst poisons. Under identical engine and exhaust conditions, two catalysts with the same overall composition may still give different results due to differences in properties such as active metal surface area, radial distribution of the active component in the catalyst, and support surface area and pore size. These useful pieces of information, needed to understand fully how a sometimes volatile, sometimes particulate poison will affect the catalyst performance, are not routinely measured as a function of time-on-stream.

The materials present in exhaust systems capable of poisoning oxidation catalysts are numerous, but fortunately most are present in small amounts. The primary poisons are lead and associated alkyl halide motor-mix components, sulfur, phosphorus, and zinc. Additional materials such as alkali metals and magnesium are occasionally mentioned as potential poisons, but the data available[34] indicate them to be only minor problems. In actual operation with noble-metal oxidation catalysts, however, the list can be shortened considerably. Under ordinary conditions of oil consumption (1 qt/1000 mi), the amount of zinc "seen" by the catalyst is not sufficient to be an important factor in poisoning. Phosphorus introduced from lubricating oil or as a fuel additive presents more of a problem[34,39] but this is not so serious a problem as posed by the presence of lead in the fuel. To serve as a point of reference, the total emissions of Pb, S, and P passed through a converter during 50,000 miles are given in Table 12.

The general effects of the major poisons, lead, sulfur, and phosphorus, have been summarized in an earlier report.[26] Aside from the current controversy concerning the effects of Pb vis-a-vis scavenger poisoning, the more recent data made available to the Panel are in general agreement with the information contained in the previous report. Each poison is considered separately.

Sulfur - At low temperatures sulfur can poison the oxidation activity of noble metals. However, under normal operation with sulfur contents of 0.03 wt% in the fuel, sulfur is not an active poison[2,25,35] provided long-term accumulations are prevented. These can be avoided by attaining catalyst temperatures of about 1400°F from time to time. Sulfur is a much more severe poison for base-metal catalysts. At the above-mentioned sulfur level in the fuel, no base-metal catalyst has consistently met the hydrocarbon standards (0.41 g/mi) for significant mileage; however, in one case a base-metal catalyst promoted with less than 0.01 wt% noble metal met the standards for over 10,000 miles.[32]

Phosphorus - Phosphorus, even in relatively small quantities, is a permanent poison for all types of oxidation catalysts. It has recently been shown that phosphorus (0.32%), added to ashless engine oil, increased catalyst deactivation during a test over 30,000 miles.[34] This represents exposure at about three times the rate indicated in Table 12 and substantiates earlier data[36] showing the poisoning of oxidation catalysts by P in the fuel. However, it is the consensus of automobile and catalyst manufacturers alike that P at current levels in fuel and oil, given reasonable rates of oil consumption, does not deactivate oxidation catalysts. In fact, in one case[2,4] it was noted that there seems to be some lessening of Pb sensitivity in the presence of phosphorus. This could be due to the formation of lead phosphate which has little poisoning activity.

Lead (and halide scavengers) - The severity of poisoning may depend strongly upon the physical and chemical state of the poison when it reaches the catalyst, and these factors make it extremely difficult to establish exactly the origin of poisoning of oxidation catalysts by lead-containing fuels. For example, lead and sulfur

TABLE 12

Total Amounts of Primary Poisons Passed Through Catalytic Converter in 50,000 Miles

Oil Component (wt%)[a]	g/50,000 miles
P (0.13)	54
S (0.35)	145
Sulfated Ash 1.3	540
Fuel Component[b]	
P (0.01 g/gal)	50
S (0.03 wt%)	4140
Pb (0.05 g/gal)	250

[a]Consumption - 1000 mi/qt
[b]Consumption - 10 mi/gal

separately may be expected to influence catalyst performance differently than when mixed together in such a way that they can form lead sulfate. Furthermore, the temperature, length, and condition (whether fresh or corroded) of the manifold and exhaust pipe leading to the converter may determine whether the poison is volatilized or present as small (or large) particles. Thus, a complete understanding must take into account all these physical parameters, as well as chemical knowledge of the poison and the poison-active site interaction.

Lead, a frequently accused poison of catalysts, has been observed in exhaust systems as lead oxide (PbO), lead sulfate ($PbSO_4$), lead phosphate ($Pb_3(PO_4)_2$), lead oxysulfate ($PbSO_4$-PbO), and lead chlorobromide ($Pb(Cl,Br)_2$).[37] The Panel has not seen a definitive analysis of the poisoning of catalysts by individual, well-defined lead compounds. Actually, the surface poison moiety, as has been shown repeatedly in other surface studies in corrosion, catalysis and epitaxy, may be a two-dimensional compound that has no three-dimensional analog.

The most complete, comparable data available concerning the joint and separated effects of lead and various halide scavengers are from Chrysler[38] and Exxon[31]. In these dynamometer-aging studies, large amounts of lead and/or halides were passed over the catalysts and the effects on HC and CO oxidation monitored. Since the conditions of both catalyst-aging and catalyst-activity measurement are important, the details of each study are summarized below.

Chrysler:[38]

Type I aging - 3 g Pb/gal (except Pb + $EtCl_2$ at 2 g Pb/gal). Schedule: 45 sec at 2400 rpm, 15 sec at idle. Typical inlet: 1-1.5% CO, 4-5% O_2, bed temperature about 1050°F. Activity measured at T = 1000-1100°F, 1-1½% CO.

Type II aging - same fuels. Schedule: 3300 rpm (48 min at 0.2% CO, 2% O_2, bed temperature about 1550°F); 12 min at 2% CO, 0-0.1% O_2, bed temperature about 1400°F; Activity measured at T ≅ 1200°F, 2% CO.

Catalyst - Pt/Pd on alumina washcoat over monolith, Chrysler manufactured.

Exxon:[31]

Dynamometer aging at rpm equivalent to 40 mph cruise, space velocity 55,000 hr^{-1} over each catalyst, catalyst mid-bed temperature about 1200 °F. Fuel 3.5 g Pb/gal + 50% halide excess except where indicated. The two catalysts were Engelhard PTX-IIB (Pt/Pd) and Engelhard PTX-A (Pt only), both supported on ceramic monoliths. Aging times were 7-10 hours on modified fuel (15-20 gal) followed by return to the original "unleaded" fuel.

These tests are of interest because they relate to typical average catalyst-bed temperatures during vehicle operation and because the poisoning derives from actual engine emission products, not from a synthetic exhaust. The two sets of data are compared in Table 13. There is general agreement on most points, with one glaring but critical exception involving the effect of Pb vis-a-vis Pb + $EtCl_2$.

With halide scavengers only (no lead present), both sets of data show similar results, as indicated below.

1. Bromine-containing exhausts will seriously deactivate Pt/Pd catalysts for both CO and HC oxidation.
2. Chlorine is a much weaker poison of such oxidations.

TABLE 13

Comparison of Exxon and Chrysler Lead Poisoning Data

Additive Package[a]	Chrysler Data/Exxon Data: Loss of %CO Conversion, Temporary	Loss of %CO Conversion, Permanent	Loss of %HC Conversion, Temporary	Loss of %HC Conversion, Permanent
TEL + EDC + EDB	69/55	7/5	52/47	16/17
TEL + EDC + EDB	--/10	--/10	--/30	--/19
TEL + EDC[c]	3/11	2/3	0/46	2/33
TEL + EDB	95/70	10/0	76/64	20/13
TEL[b]	(1-5)/2	5/1	0/9	7/9
EDB + EDC	90/67	2/0	54/37	16/0
EDB + EDC	--/5	--/0	--/12	--/0
EDB	55/56	2/0	46/52	8/4
EDC	0/0	0/0	0/13	3/5

[a] 3.5 g Pb/gallon + 1.5 theory scavenger(s) (Exxon)
3.0 g Pb/gallon + 1.0 theory scavenger(s) (Chrysler)

[b] 2.0 g Pb/gallon (Exxon)

[c] 2.0 g Pb/gallon + $EtCl_2$ (Chrysler); Chrysler dynamometer conditions unspecified.

Poisoning time: 7-10 hours (Exxon), 10 hours (Chrysler)

TEL - tetraethyllead
EDC - ethylenedichloride
EDB - ethylenedibromide

REFS. 31, 38

3. Halide catalyst poisoning is largely or completely reversible on removal of the halide from the exhaust, even within the time scale of these experiments (a few hours).
4. Comparison of the Pt/Pd results and the Pt results suggests that Br attacks primarily Pd.

When lead compounds (TEL) are present in the fuel, the results (including the point of disagreement) can be summarized by the following statements.

1. TEL alone in the fuel results in lesser deactivation than TEL + halide scavengers. (What fraction of this unscavenged lead actually reached the catalyst is not established since neither group performed lead material balances on their systems.)
2. Pt/Pd catalysts appear to recover more completely than Pt-only catalysts, but they are poisoned more easily, especially for CO oxidation. (This is consistent with other data showing susceptibility to poisoning of Pd vs. Pt in the presence of lead + motor mix.[32,39,40]
3. With the exception of the Chrysler data for TEL + ethylene dichloride, all results indicate a greater permanent activity loss for hydrocarbons in the presence of lead (and scavenger) than in the presence of scavenger only.
4. It appears that one might infer (perhaps incorrectly) that the catalyst itself recovers its CO oxidation capacity more easily than its HC oxidation ability. Since CO oxidation on a new catalyst is much more rapid than HC conversion, the recovery of any appreciable fraction of catalyst activity will bring CO conversion back to a very high level. In other words, since <u>all</u> of the catalyst is needed for HC (but not CO) oxidation, HC oxidation recovery is the key to catalyst poisoning detection.

Based on these data alone, it is not possible to resolve the Chrysler vs. Exxon differences for hydrocarbon oxidation with tetraethyl lead plus ethylene dichloride in the fuel. <u>The central point of</u>

difference is that Chrysler sees little, if any, activity loss, whereas Exxon reports a substantial activity loss, both temporary and permanent.

In an attempt to resolve these differences, General Motors[41] recently conducted some experiments on both bench-scale apparatus and automobiles. In general, their results confirm the Exxon data and contradict the Chrysler results. Their data plotted in Figure 12 clearly confirm that ethylene dibromide by itself is a temporary poison (in agreement with both Chrysler and Exxon). Similar tests showed that ethylene dichloride had a smaller temporary effect. However, Figure 13 indicates extensive poisoning with TEL + EDC, in sharp contrast with the Chrysler data in Figure 14. Notice that the poisoning was apparently irreversible (within the time frame of the experiment). Unfortunately, General Motors did not report tests with pure TEL in the absence of any scavengers.

To explain the contradictory results, General Motors[41] suggested that interference of lead compounds deposited on the insides of the exhaust pipes in the absence of scavengers could be removed and transported to the catalyst when the scavengers were introduced. They offered experimental evidence to support this claim. However, this does not help resolve the discrepancies between the Chrysler vs. General Motors and Exxon data.

While more work is obviously necessary to clarify this issue with complete certainty, the members of the Panel of Consultants are convinced that under most conditions, lead, when it reaches oxidation catalysts, acts as a permanent poison. It may be slowly desorbed in some form during prolonged treatment in unleaded streams at high temperature, but it also diffuses into the catalyst structure. It is doubtful that oxidation catalysts once poisoned by lead will ever regain their full unpoisoned activity.

There are numerous reports that catalyst deactivation is directly related to the amount of lead on the catalyst,[36,37,39-49] although most of these tests were carried out in the presence of scavengers. But lead deposits are seldom uniform throughout the

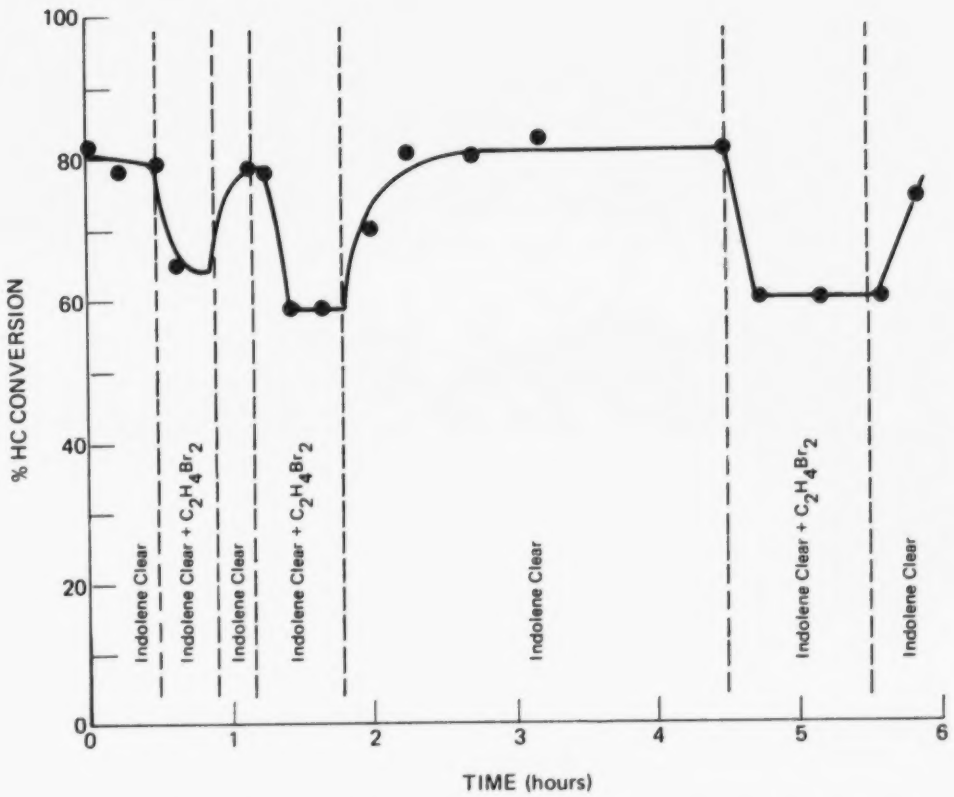

FIGURE 12 Effect of Bromide Scavenger on HC Activity in Lead-Free System. Catalyst: Pt-Pd; Scavenger: 1.4 g $C_2H_4Br_2$/gal; Inlet Temperature: 565°C; GHSV: 128,000 hr^{-1}.

REF. 41

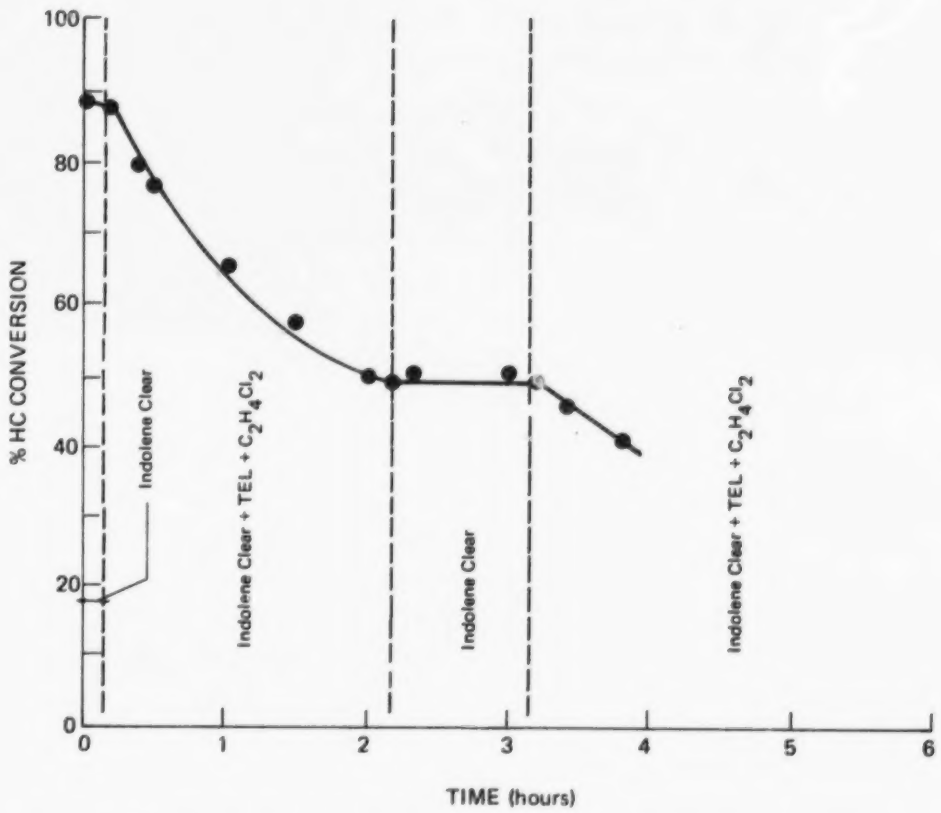

FIGURE 13 Effect of TEL and Chloride on HC Activity. Catalyst: Pt-Pd; Fuel Additive: 3 g Pb + 2.8 g $C_2H_4Cl_2$/gal; Inlet Temperature: 565°C; GHSV: 128,000 hr^{-1}.

REF. 41

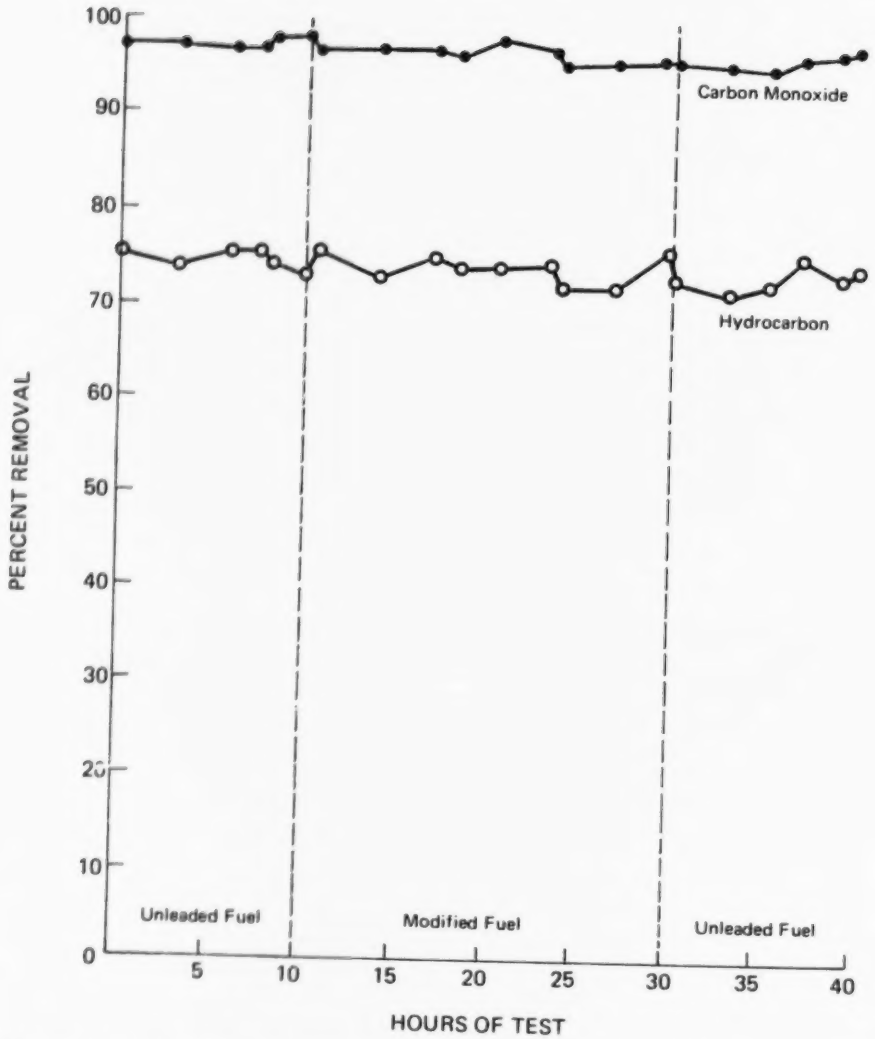

FIGURE 14 Oxidation Catalyst Poisoning Test - Effect of Fuel Containing Tetraethyl Lead and Ethylene Dichloride. Unleaded Fuel: MS 3900A; Modified Fuel: MS 3900A at 2.0 g/gal Pb Plus 1.0 T Ethylene Dichloride.

REF. 38

catalyst bed, and the deposition is a function of several system parameters. With a monolithic catalyst, Daimler-Benz AG (Mercedes) showed that the deposition of Pb at the entrance of the bed passes through a maximum as a function of temperature, as shown in Figure 15.[50] Klimisch, et al.[40] have examined the distribution of lead in a poisoned pelleted catalyst and also found changes that depend on temperature. Figure 16a shows that the Pb is concentrated mainly on the external surface of the pellet under normal operation, but Figure 16b shows that it becomes more homogeneously distributed throughout the pellet after treatment in O_2 at 900°C. It is not surprising, then, that the position of the catalyst bed has a significant effect on the susceptibility to poisoning. As the catalyst is moved further downstream from the exhaust ports, more lead is deposited.[51] While the degree of catalyst deactivation varies with fuel lead levels at all locations, the influence per gram of lead deposited diminishes as the catalyst position is moved further from the engine. This may be explained by the lead being deposited as particles which may be larger in size the further from the engine and thus tend to remain at the external surface of the catalyst. Other chemical factors such as the interaction with sulfur oxides (perhaps to form lead sulfates) may affect the poisoning behavior, and such formation has been advanced by Chrysler[38] to account for the decrease in SO_3 emissions in the presence of lead. Other interactions with such exhaust components as oxygen, phosphorus, halides, etc. could be discussed, but most of these would be in the realm of speculation and will not be treated.

E. Poisoning of NOx Catalysts

The base-metal systems of Questor and Gould appear to be quite resistant to chemical poisons, not because of any inherent superiority of the ingredients in this respect, but because of the very high temperatures of operation involved. However, addition of the upstream "oxygen getter" catalyst, which is a conventional oxidation catalyst containing noble metals, and the downstream oxidation catalyst make the

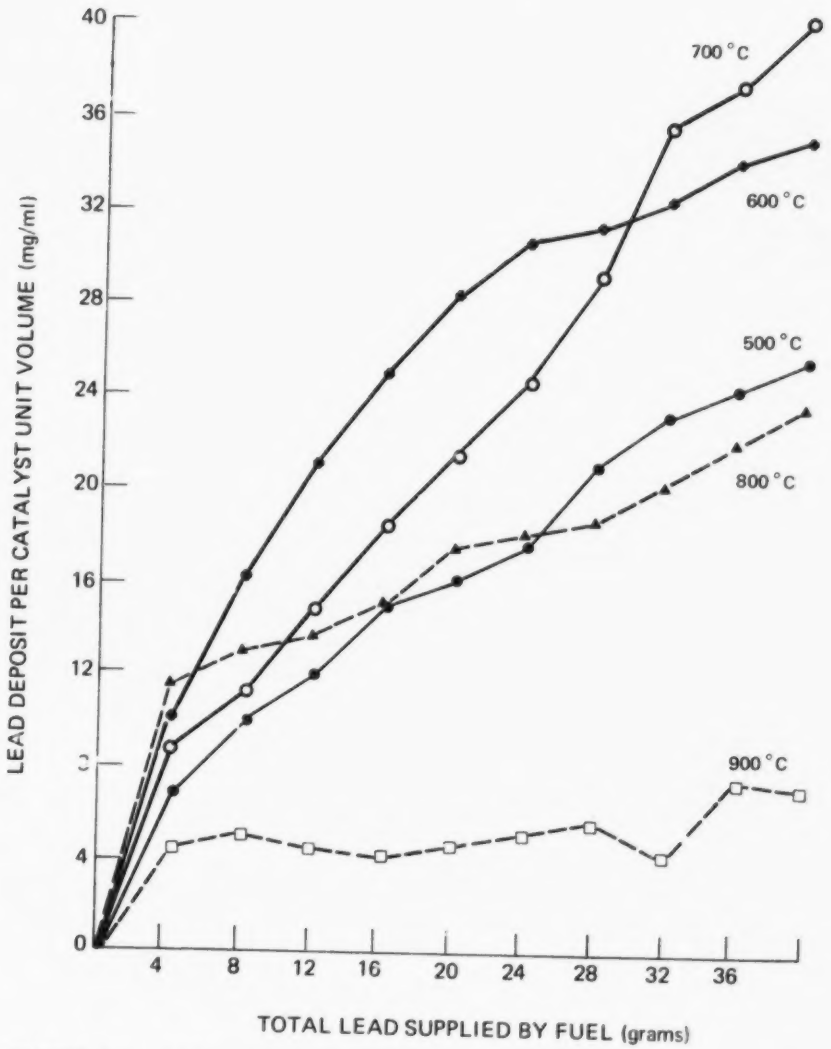

FIGURE 15 Lead Deposits at Entrance of Catalyst Over Lead Content in Fuel as a Function of Gas Temperature.

REF. 50

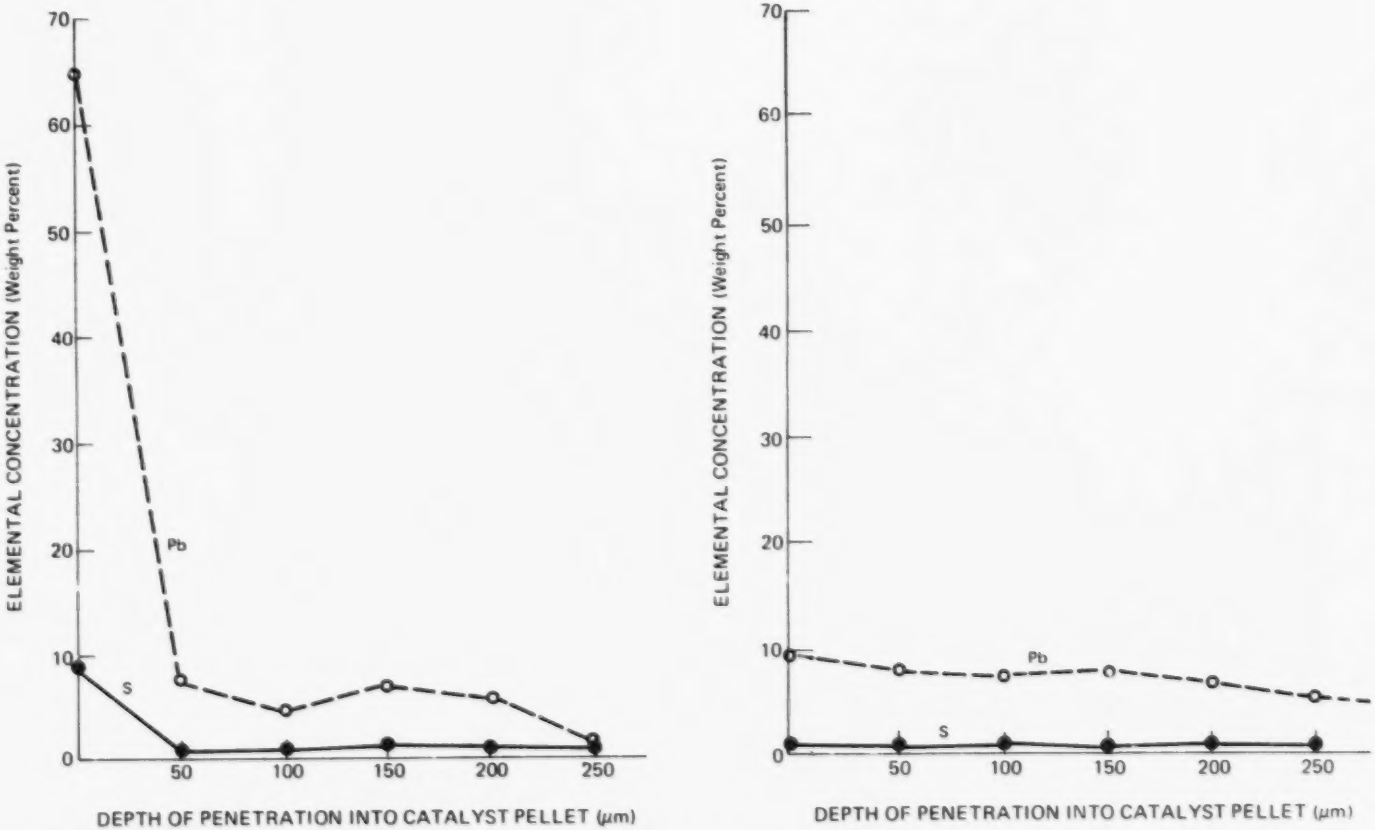

FIGURE 16 Lead and Sulfur Distribution in Lead-Poisoned Catalyst Pellet. Right-Hand Graph: After Exposure for 100 hr to Exhaust from an Engine Using 0.5 g/gal Pb in Fuel. Left-Hand Graph: After "Regeneration" in Air for 90 hr at 900°C.

REF. 40

Gould GEM-68 system subject to poisons. Other types of NO_x catalysts--the Ru formulations, noble metal-base metal combinations, and the three-way catalysts--again are susceptible to the "big three" poisons of lead, phosphorus, and sulfur. Generally, the effect of these poisons is very similar to that on oxidation catalysts[2,29] if measured in terms of total activity loss. Some quantitative data on the susceptibility of ruthenium catalysts to the combined effects of Pb and S under both oxidizing and reducing conditions are shown in Figure 17[4]. (Note that there is some variation in space velocities in these figures.) It is seen that these formulations are much more severely affected by Pb and S under oxidizing rather than reducing conditions. However, in order to meet combined HC/CO/NO_x standards, the selectivity as well as the activity of the catalyst must be maintained. Maintenance of selectivity seems to be a major problem given the current status of NO_x catalyst development. A persistent difficulty seems to be the selective deactivation of HC oxidation activity while operating under conditions that decrease NO_x emissions. These troubles are particularly notable with three-way systems. Some typical data on changes of selectivity in a three-way system are shown in Table 14.[2]

As is evident from the general nature of the comments above, very little information specific to the effect of individual poisons on NO_x systems is currently available. There are, however, more data available on overall durability of NO_x catalysts systems, which is discussed in the following section.

F. Long-Term Durability

Oxidation catalysts - Most automobile manufacturers who intend to sell cars in the U.S. have developed systems with noble-metal oxidation catalysts that will last 50,000 miles when run on EPA durability fuels, and most have vehicles that are now in the final stages of certification for the 1975 interim standards. Furthermore, several of the companies have met the ultimate 3.4 (CO) and 0.41 (HC) g/mi standards for 50,000 miles. All these systems have been operated on

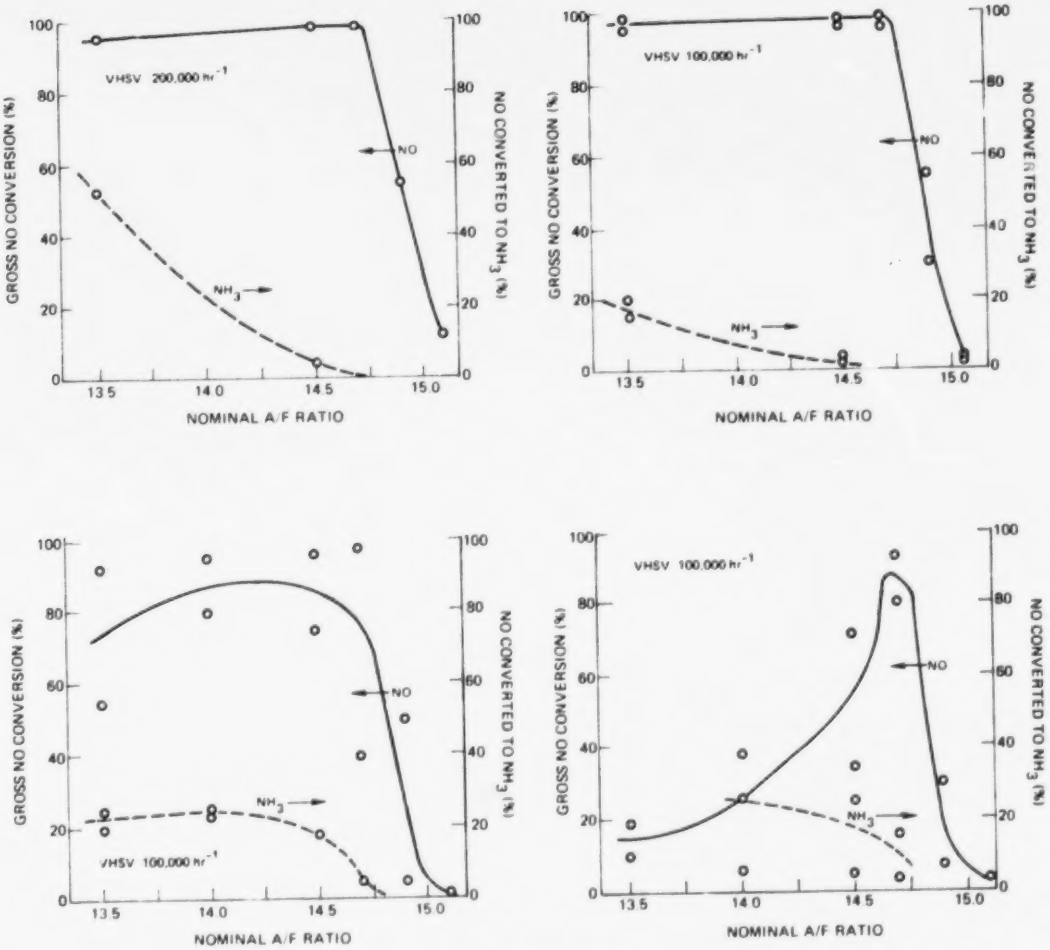

FIGURE 17 Effect of Pb and S on Stabilized, Supported Ru Catalysts for Removal of NO from a Synthetic Exhaust in an Oxidizing and Reducing Condition. Test Conditions on Laboratory Unit: 500°C and VHSV as Noted. Engine Aging Conditions on Dynamometer and Fuel as Follows: a) Virgin Catalyst; b) Lead Sterile Fuel for 60 hr, 10% Oxidizing (15/1 A/F); c) Durability Fuel (0.035 g/gal Pb, 340 ppm S) for 60 hr; and d) Durability Fuel for 60 hr, 10% Oxidizing (15/1 A/F) Plus 8 hr Oxidizing (16.4/1 A/F).

REF. 4

TABLE 14

Selectivity Characteristics of Three-Way Catalysts

Engine Dynamometer Activity Test (1200°F)

Supplier	Ford Code	Steady State Selectivity									
		Fresh					Aged 100 Hours				
		% Gross NO_x	% NH_3	% CO	% HC	Inlet CO/O_2	% Gross NO_x	% NH_3	% CO	% HC	Inlet CO/O_2
1	M152C3-1*	78	2	78	78	1.5	35	0	35	35	1.6
	M152C3-1 & 2**	98	0	86	90	1.0	80	0	74	66	1.8
2	M196-19*	80	2	80	68	1.4	64	3	63	66	1.3
	M196-19 & 20**	92	0	84	80	1.8	85	2	82	86	1.7
3	M226L1-1*	92	0	84	82	1.2	16	1	15	15	1.6
	M226L1-1 & 2**	90	0	89	92	2.6	56	0	52	60	1.4
4	M227L1-1*	72	2	70	58	2.2	22	6	16	16	2.2
	M227L1-1 & 2**	80	0	70	80	2.0	-	-	-	-	-
5	DN-1*	84	2	80	74	1.0	53	0	53	53	1.2
	DN-1 & 2**	82	0	82	82	1.8	78	0	81	73	1.2

*Single Element Converter (130,000/Hr Space Velocity)

**Tandem, Two Element Converter (65,000/Hr Space Volocity)

REF. 2

the lean side of stoichiometry at the catalyst inlet, this being accomplished by some with and some without the addition of an air pump. Future expected improvements in the catalyst will probably involve a decrease in the amount of noble-metal loading through better dispersion and/or the addition of amounts of base metals.

NO_x catalysts (three-bed systems) - The only serious durability study now in progress is the Gould GEM-68 system with three catalysts (an oxygen "getter" - ½ PTX monolith, a GEM-68 base-metal monolith NO_x catalyst, and a PTX oxidation catalyst) and operated on the rich side of stoichiometric. On a Ford vehicle this system now (7-9-74)[52] has accumulated 25,100 miles with the last reported emissions as follows: 0.48 (HC), 3.7 (CO), and 0.55 (NO_x) in g/mi. Even though the car has not been "optimized" to give the lowest possible emissions, all emissions curves have been essentially flat, thus indicating no gross deterioration. Similarly, a Datsun car has been shown to meet the 0.4 NO_x standards for 25,000 miles. To the Panel of Consultants' knowledge, no U.S. auto manufacturer has tested the GEM-68 getter system.

Three-way catalysts - Development in this area appears to have diminished continually since two years ago. However, the recent general concern about both fuel economy and the lack of well-established NO_x catalyst systems has renewed serious three-way development programs. With a few exceptions, communication channels between the manufacturers of O_2 sensors and of three-way (or other) catalysts do not appear to be as well developed as might be desired.

Overall durability of HC/CO/NO_x systems - With presently developed NO_x systems (single-bed, dual-bed, triple-bed), the prospect of simultaneously meeting the 0.41/3.4/0.4 HC/CO/NO_x standards over a 50,000-mile cycle are poor. This statement refers to the current status of all manufacturers visited.

Data typical of performance on small-engine displacement vehicles with dual-bed systems are given in Figure 18.[29] While there is some difference in the rate of deterioration determined for the various catalysts evaluated, it would appear that most, if not all, of these

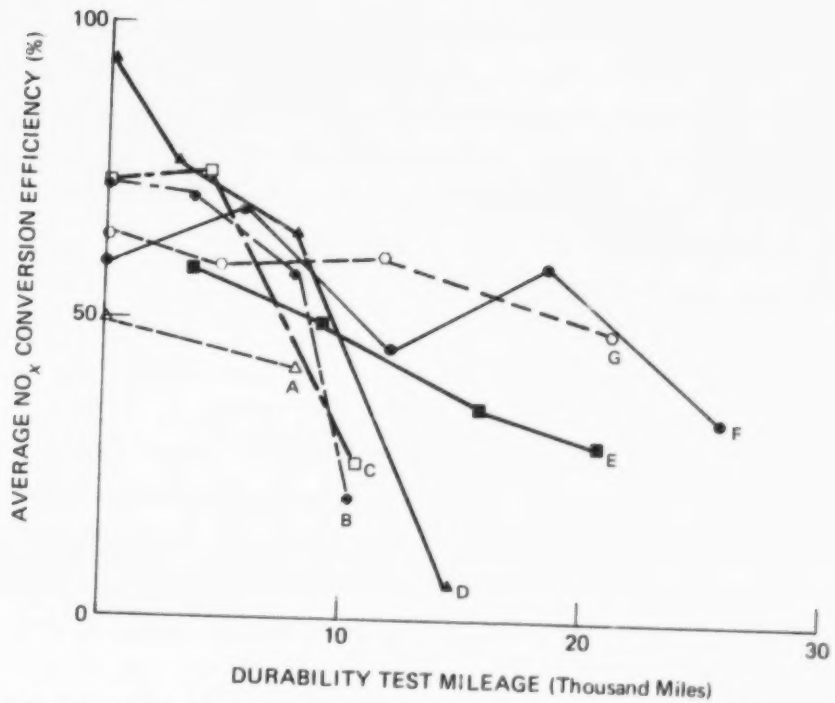

FIGURE 18 Durability Test Results of Some NO_x Catalysts for a Small Vehicle (Datsun P610, 2750 lb). Average Conversion Efficiency Measured During CVS-CH Test After Maintenance. Mileage Accumulated on Modified AMA Durability Cycle.

REF. 29

systems would exhibit zero NO_x conversion efficiency well before attaining 50,000 miles. Corresponding typical durability data for dual-bed systems on larger displacement vehicles are shown in Table 15[2] and in Figures 19[2] and 20.[25] Again, there is a substantial deterioration of activity over test mileages much less than 50,000; in Figure 19,[2] the NO_x standard of 0.4 g/mi is not met over any portion of the test cycle, although one catalyst (from Nippodenso) exhibited durability for 24,000 miles as seen in Figure 20.

One extremely important point is that control of the NO_x cannot be separated from HC/CO control. For example, an engine tuned to run fuel rich (as is required for NO_x reduction) necessarily increases the concentrations of HC and CO in the exhaust and thus puts an increased burden on the oxidation catalyst. The effect of NO_x control on the concentration of CO in the exhaust is shown in Figure 21;[25] similar data are available for HC. This can result in premature failure of an oxidation catalyst that would be completely adequate for an engine tuned for HC/CO control alone. Furthermore, should the oxidation catalyst fail in such a system, the pollution would be considerably increased over the levels that would occur and be observed as a result of failure in a HC/CO-only catalyst system.

While dual- (or triple-) bed systems may be developed to the point where they will be effective for 50,000 miles, the prospects are not bright. Furthermore, the fuel-economy penalty inherent in such systems due to rich operation, the additional noble-metal requirement for more than one catalyst bed, the increased demands on the oxidation catalyst, and the pollution consequences of oxidation-catalyst failure are substantial hurdles that must be considered for such systems.

For three-way catalyst systems, deterioration of the catalyst is coupled with deterioration of the sensor, as has been mentioned previously. Some durability results obtained with a small displacement vehicle (2 liter, 3500 lb inertial weight) using the Bosch sensor-fuel injection system are shown in Figure 22.[29] The major

TABLE 15

Summary of NO_x Catalyst Durability for Ford Vehicles

A total of eleven monolithic NO_x catalysts have been durability testing in vehicles. In some of the vehicle tests, independent exhaust systems were installed on each bank of the V8 or V6 engine allowing concurrent evaluation of two different NO_x catalysts. All data obtained from these tests are summarized below.

Vehicle	Catalyst	Effective Total NO_x Catalyst Volume (Cu In.)	Inertia Weight (Pounds)	Feed-gas CVS-CH NO_x (g/mi)	Miles Accumulated	CVS-CH NO_x Efficiency "0" Miles/ Terminal Miles
21A91-D 429-4V A/T Galaxie	Ford (M-177B)	84	5,000	0.96	12,000	53/31
11A55-D 351W-2V A/T Galaxie	Corning (M-117)	168	5,000	2.40	21,000	78/44
22C58-D 2.6L A/T Capri	Ford (M-177) Noble Metal	72	2,750	2.20*/	12,000	78*//25*/
	Ford (M-176B) Noble Metal	72	2,750	2.20*/	12,000	79*//15*/
31A73-D 400-2V A/T Galaxie	Ford (M-190) Noble Metal	84	5,000	1.27	12,000	73/20
31A74-D 400-2V A/T Galaxie	AMOCO (DA) BM/NM	84	5,000	1.05	12,000	64/32
11A55-D 351W-2V A/T Galaxie	AMOCO (DB) Base Metal	168	5,000	3.08	21,000	77/56
	Gulf (M-166)	168	5,000	2.06	22,000	67/47
110T714 351W-2V A/T Galaxie	Ford (M-190) Noble Metal	84	5,000	1.69	25,000	72/40
110T718 429-2V A/T T-Bird	Union Oil (M-186) BM/NM	84	5,500	0.80	5,000	40/28
14A53 351W-2V A/T Galaxie	GOULD Metallic	84	5,000	2.0	3,000	91/26**

**Catalyst Failed Physically

REF. 2

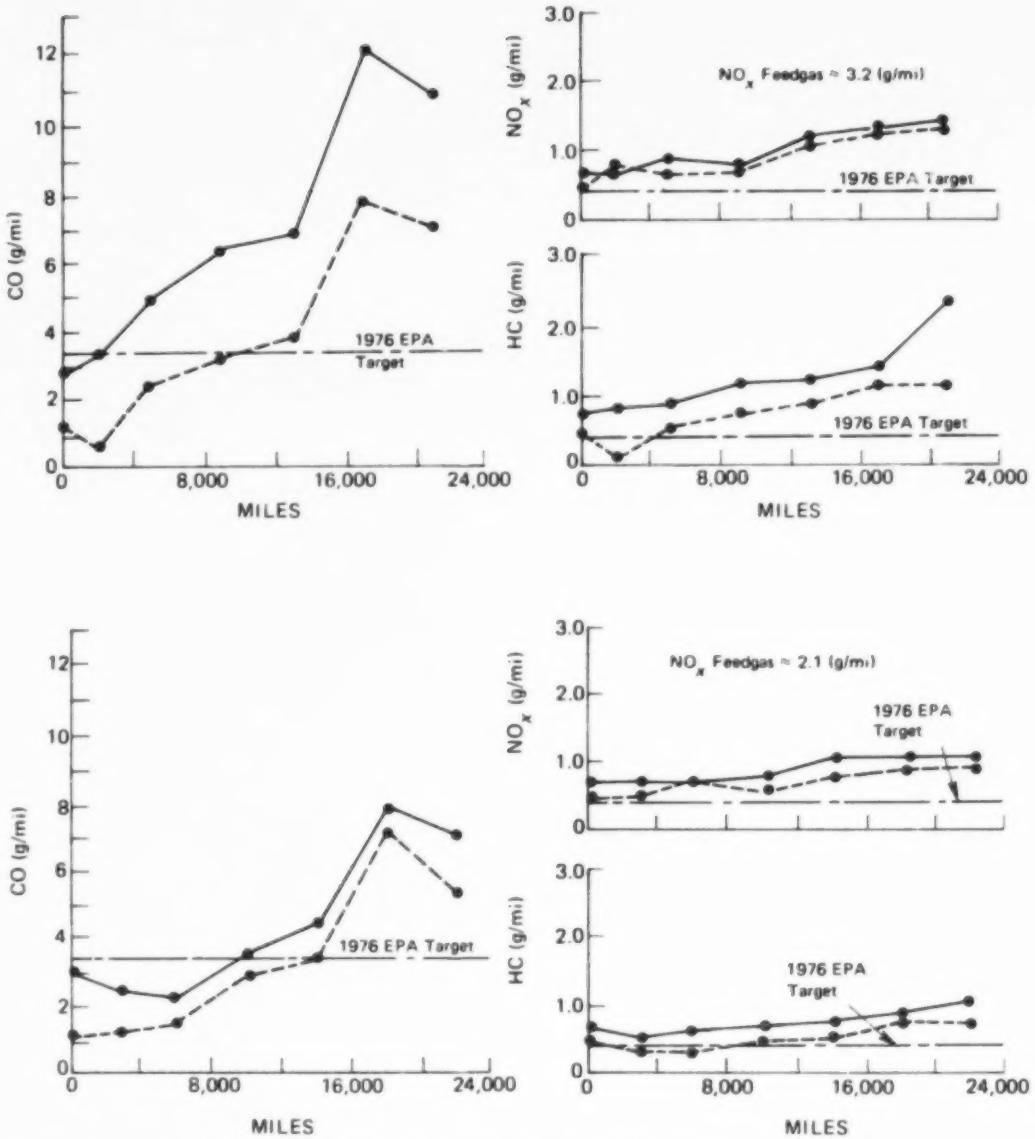

FIGURE 19 Durability Data on Ford's NO_x Catalysts. CVS-CH Emissions versus EPA Mileage. Concept Package D, Vehicle 11A55-D, 351W-2V Automatic Transmission Galaxie. HC/CO Catalyst: Aged M-21 (21,000 Miles). Solid Line: CVS-CH, Dotted Line: CVS Hot. Top Graphs: NO_x Feed Gas $\approx$ 3.2 g/mi, Bottom Graphs: NO_x Feed Gas $\approx$ 2.1 g/mi.

REF. 2

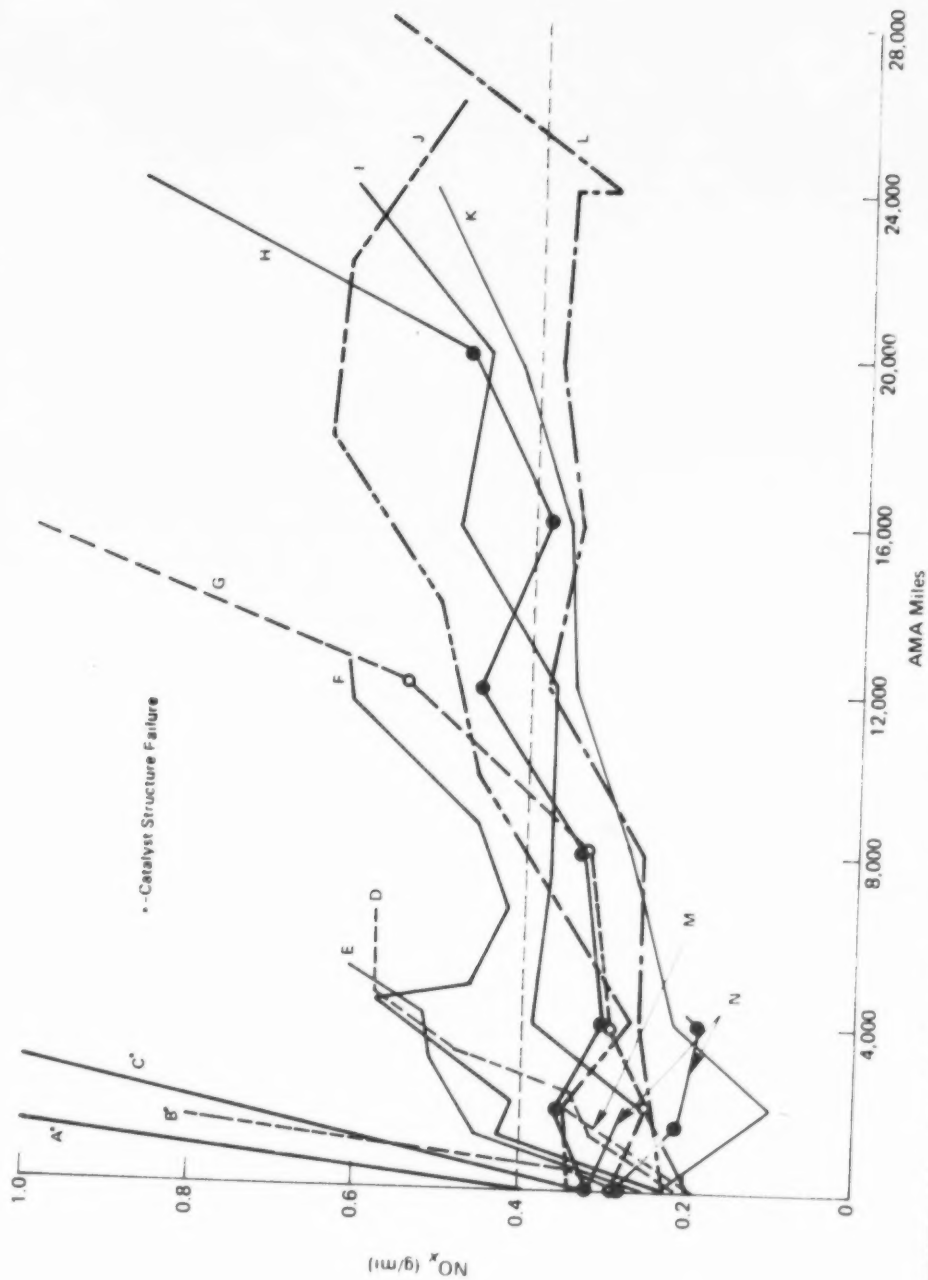

FIGURE 20 Durability Data on General Motors' NO_x Catalysts. Emission Durability Test Results, Dual Catalyst Emission Control Systems. 1975 Federal Test Procedure.

REF. 25

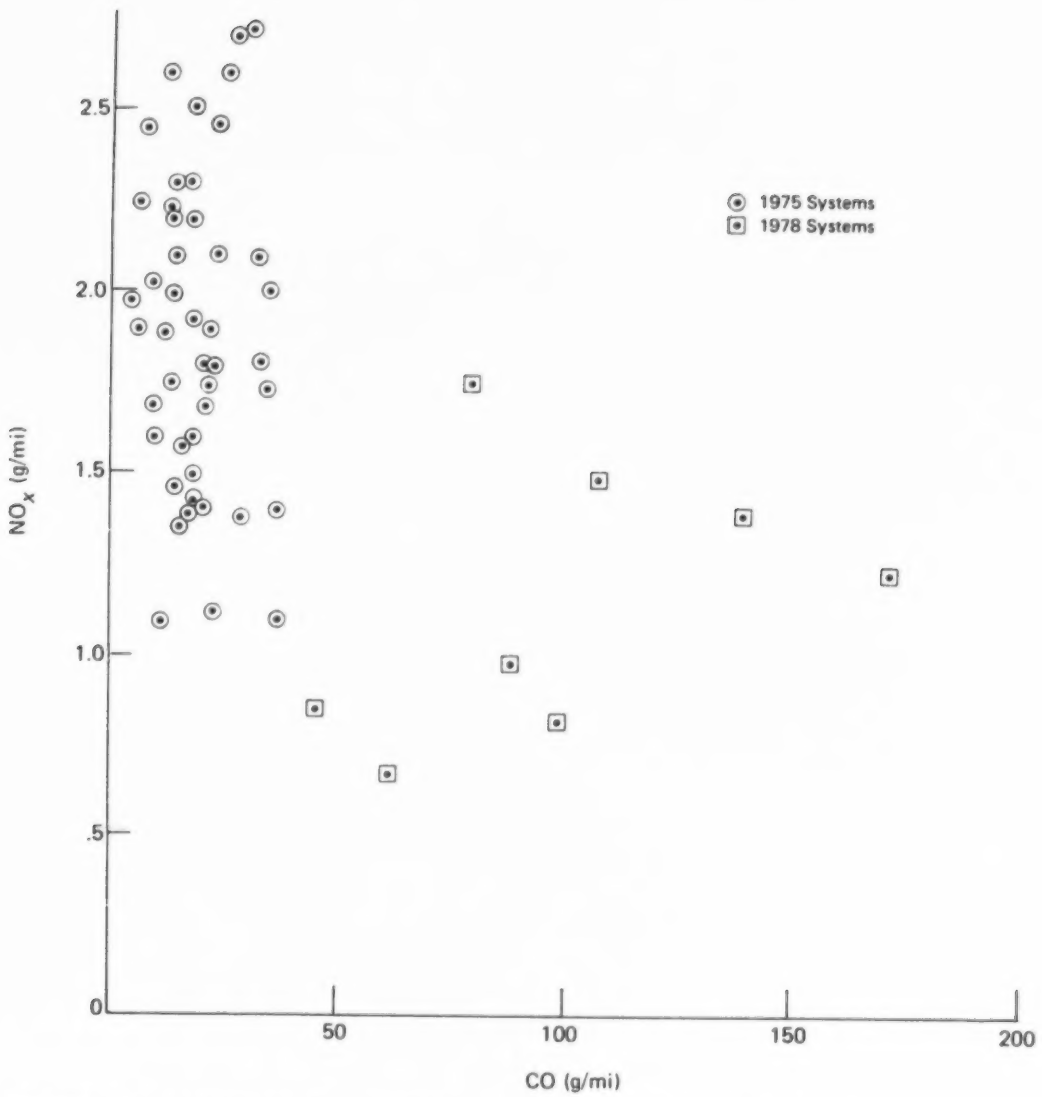

FIGURE 21 Effect of NO_x Control in Advanced Emissions Systems on CO Concentration.
REF. 25

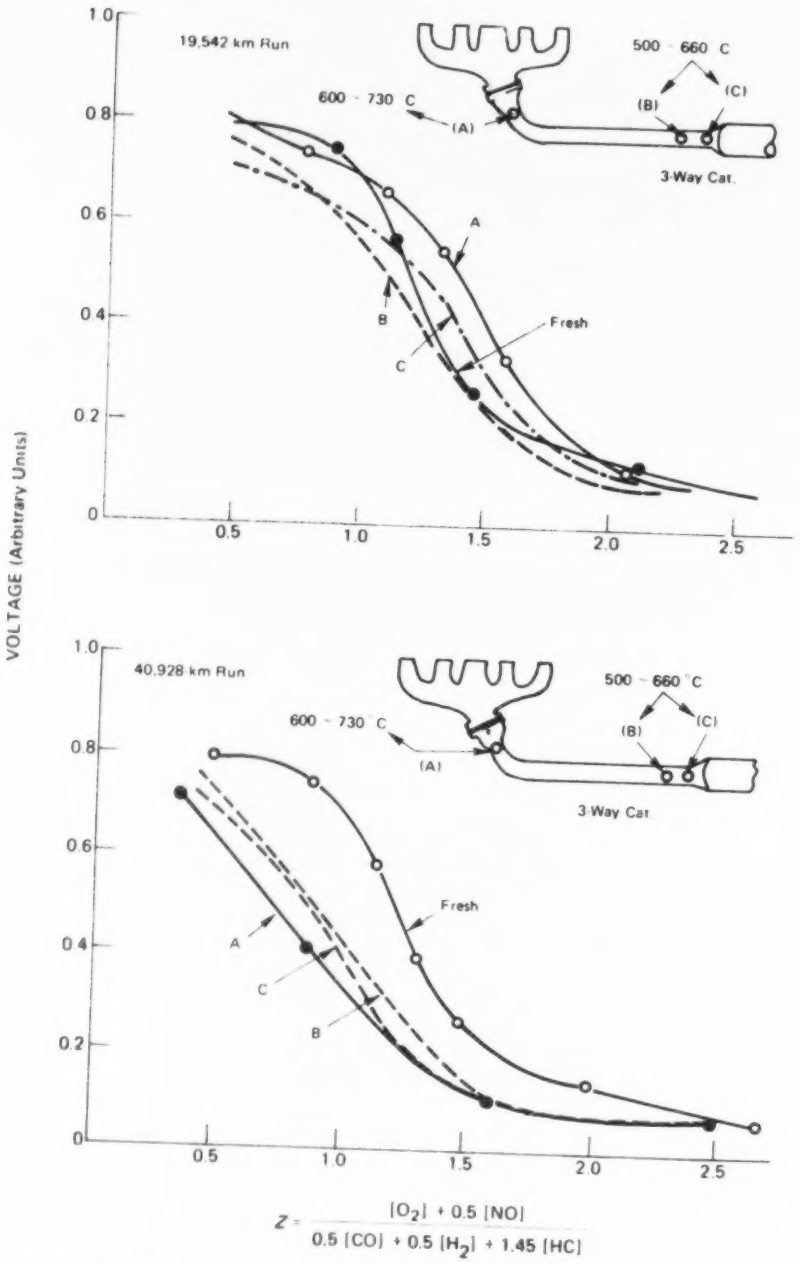

FIGURE 22 Durability Test Results of O_2 Sensor. Evaluation Conditions: Temperature 650°C (at A), 2,000 rpm, 5.3 kg m. Test Conditions: Modified AMA Temperature Durability Mileage Accumulation, Temperature Indicated at Points A, B, and C.

REF. 29

effect of deterioration on three-way catalysts is a shifting and narrowing of the operational "window" with increasing operation. This is illustrated in Figures 23 and 24 for mixed base-noble metal and noble-metal catalysts, respectively.[29] It is apparent in both cases that the operational "window" of the fresh catalyst with respect to the air/fuel ratio is considerably altered; further, it is altered in different ways for the CO, HC, and NO_x. In fact, one would conclude from the particular data shown here that the "window" is effectively destroyed by deterioration of the catalyst.

Correspondingly typical data for the alteration of the sensor response is shown in Figure 22.[29] Sensor output becomes much less sensitive to A/F ratio, and decreases in absolute magnitude, with age. For this reason, most manufacturers consider, with current technology, the effective life of the sensor to be about 15,000 miles. Even if the catalyst were still active, the sensor would require replacement about once a year. However, the device is not expensive and can probably be replaced with the same ease as a spark plug.

While the preceding statements refer to the "average" state of development of three-way catalyst systems, the Robert Bosch Company from Germany has recently indicated significant advances in this field. They claim to have catalysts and sensors that will last over 25,000 miles. General Motors has now made similar claims. In light of these developments, the three-way catalyst approach is showing much more promise than it did two years ago.

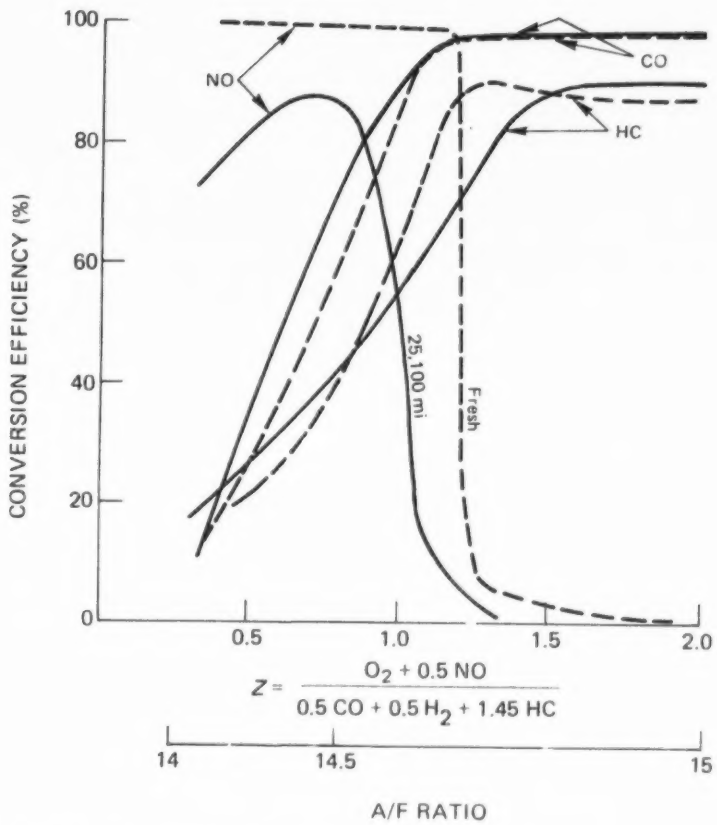

FIGURE 23 Evaluation Test Results of Mixed Noble-Base Metal Three-Way Catalyst on Monolith, Steady State. Catalyst: GC 301; Size: 4 in. D x 3 in. L x 4 in.; Durability Mileage: AMA 25,100 Miles (on Engine Dynamometer); Test Conditions: Inlet Gas Temperature - 600°C, Inlet CO Concentration - 500 ppm; Space Velocity: 60,000 hr^{-1}.

REF. 29

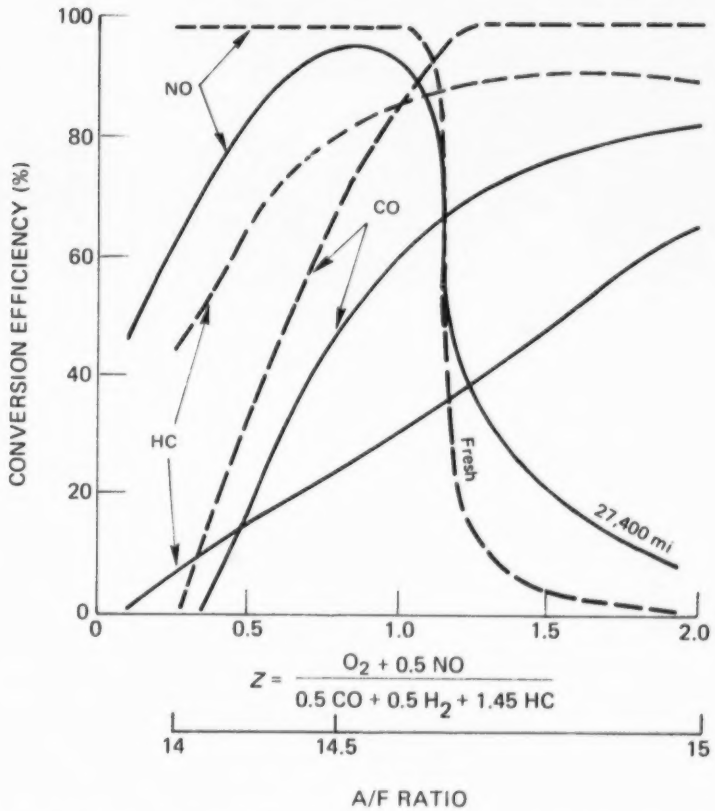

FIGURE 24 Evaluation Test Results of Noble Metal Three-Way Catalyst on Monolith, Steady State. Catalyst GD 306; Size: 4 in. D x 3 in. L x 4; Durability Mileage: AMA 27,400 Miles (on Engine Dynamometer); Test Conditions: Inlet Gas Temperature 600°C; Inlet NO Concentration 500 ppm; Space Velocity: 60,000 hr^{-1}.

REF. 29

V. MATERIALS SUPPLY AND TOXICOLOGY

Catalysts that will be used for exhaust-pollution control in over half of the new automobiles sold in the U.S. beginning in 1975 will include a small amount of noble metal (specifically platinum, palladium, rhodium, and/or ruthenium) sparsely distributed on a refractory oxide support (e.g., alumina, cordierite, etc.). Other systems currently under development make use of base metals (e.g., nickel, copper, chromium, and/or cobalt) deposited on a wire mesh made of a high-temperature, nickel-chromium alloy support (or on a refractory-oxide support) for NO_x control.

Some of these components are not produced domestically and must be imported. Furthermore, the quantities of materials required for this new application will in some cases be comparable to the total amount presently consumed in all uses. Almost all potential catalytic components are included in the government's list of strategic and critical materials.[26] This raises the issue of possible materials shortages, the first topic discussed in this chapter.

Concern has also been expressed about possible health effects of catalytic components should they be displaced from the converters and become transported into the environment. Little information exists regarding the toxicology of noble metals, but what is known is summarized in this chapter.

Finally, the effects catalysts may have on nonregulated pollutants (e.g., sulfates, nitrous oxide, and ammonia), and the associated environmental implications are discussed in this chapter as well.

A. Materials Supply

Noble metals - Within the U.S. there are no known ore deposits containing sufficiently high concentrations of noble metals that can be mined profitably. Because of this, essentially all noble metals used here must be imported. A recent review by the Southwest Research Institute[54] adequately summarizes the world supply/demand

situation for the two principle noble metals (Pt and Pd) considered for automobile application. The findings from that study are contained in Tables 16a-e. The scenario in the last table gives a reasonably realistic estimate of the future demands for noble metals through 1990, assuming the emission-control catalysts will continue to be used on U.S. automobiles. Should other countries adopt such uses, these estimates would need to be increased. However, should base metals replace noble metals as catalytic components, the figures would be too high.

As indicated in Table 16a, the two major producers of noble metals are South Africa and the U.S.S.R. with Canada a distant third. However, the relative amounts of noble metals in ores from the countries are quite different, as indicated in Table 17. While South Africa is mainly a platinum producer (Pt/Pd = 2.5), the U.S.S.R. produces primarily Pd (Pt/Pd = 0.5); in Canada the two metals are produced in about equal quantities.

Most platinum-group metals now imported into the U.S. come from South Africa, and it is not expected that this pattern will shift significantly in the next five years. For their projected needs in catalytic converters, the major U.S. automobile companies have separate contracts directly with the South African producers, although some Pd for automobiles will initially come from the U.S.S.R. General Motors has contracted with Impala for about 420,000 oz noble metals/year for 10 years, and Ford has a similar agreement with Engelhard Industries to provide 380,000 oz/year for three years (with an additional 360,000 oz in 1978) from the Rustenberg mines. Chrysler will purchase their noble metals from Impala in South Africa, although the Pd and part of the Pt for their 1975 cars has come from the U.S.S.R.

The catalyst-equipped Chrysler cars will use monoliths relatively heavily loaded with from 0.08-0.16 oz noble metals/car in a 70/30 Pt/Pd mixture. Ford also plans to use monoliths with a variety of loadings ranging from 0.03 to 0.07 oz noble metals/car in mixtures that contain 66/34 Pt/Pd and 93/7 Pt/ (some other noble metal, probably Rh). General Motors will use pelleted catalysts in two sizes of converters, each

TABLE 16

Supply/Demand Picture for Platinum and Palladium

a. WORLD PRODUCTION OF PLATINUM & PALLADIUM

Average Annual, 1969-1972
(Thousands of Troy Ounces)

Source	1969-1972 Average Platinum	Palladium	Total
Canada	188	187	375
Colombia	26	-	26
Ethiopia	0.3	-	0.3
Finland	0.2	0.3	0.5
Japan	3	5	8
Philippines	0.6	1	1.6
Republic of South Africa	909	321	1230
U.S.S.R.	665	1339	2004
United States	9	13	22
TOTAL	1801	1866	3667

Sources: Minerals Yearbook and Engineering and Mining Journal.

b. WORLD CONSUMPTION OF PLATINUM & PALLADIUM

1971
(Thousands of Troy Ounces)

Nation	Consumption
United States	1376
Japan	758
U.S.S.R.	589
West Germany	451
France	313
Italy	74
Canada	68
United Kingdom	49
Netherlands	33
Sweden	17
Switzerland	12
TOTAL	3740

Source: Minerals Yearbook.

c. PLATINUM AND PALLADIUM SALES TO U.S. INDUSTRY

1967-1971 Averages
(Thousands of Troy Ounces per Year)

Industry Category	Five-Year Average Annual Sales: Platinum	Palladium	Total
Electrical	97	389	486
Chemical	155	208	363
Petroleum Refining	184	9	193
Dental and Medical	23	56	79
Glass	49	5	54
Jewelry and Decorative	31	19	50
Miscellaneous	29	35	64
TOTAL	568	721	1289

Source: Minerals Yearbook.

REF. 54

TABLE 16 (continued)

d. WORLD RESERVES PLATINUM & PALLADIUM

1970 Estimates
(Thousands of Troy Ounces)

Nation	Reserves		
	Platinum	Palladium	Total
Republic of South Africa	142,400	50,200	192,600
U.S.S.R.	60,000	120,000	180,000
Canada	6,940	6,860	13,800
Colombia	5,000	-	5,000
United States	950	1,960	2,910
TOTAL	215,290	179,020	394,310

Source: Mineral Facts and Problems, 1970.

e. ESTIMATED FUTURE WORLD DEMAND PLATINUM & PALLADIUM

(Thousand of Troy Ounces per year)

		Total Demand		
		1971	1980	1990
United States:	base platinum	541	734	1044
	automotive catalysts		774	866
	total platinum	541	1508	1910
	base palladium	760	898	1095
	automotive catalysts		332	371
	total palladium	760	1230	1466
	total base	1301	1632	2139
	total automotive		1106	1237
	Total	1301	2738	3376
Rest of world:	platinum	1283	1826	2703
	palladium	1163	1655	2450
	Total	2446	3481	5153
Grand total:	platinum	1824	3334	4613
	palladium	1923	2885	3916
	Total	3747	6219	8529

Source: Mineral Facts & Problems, 1970; A Look at Business in 1990 (a Summary of the White House Conference on the Industrial World Ahead. February 7-9, 1972); and SwRI.

REF. 54

TABLE 17

Estimated Composition of Noble Metals from Different Sources

Metal	Percentage by Weight		
	Canada	U.S.S.R.	South Africa
Platinum	43.4	30	64.02
Palladium	42.9	60	25.61
Iridium	2.2	2	0.64
Rhodium	3.0	2	3.20
Ruthenium	8.5	6	6.40
Osmium	---	-	0.13

REFS. 54,55

with 0.05 oz noble metals/car in a 71/29 Pt/Pd mixture. American Motors will use similar converters on their cars. On the average, it appears that cars with oxidation catalysts in 1975 will contain between 0.05 and 0.07 oz noble metals/car. Probably about 75% of the domestically produced cars will be equipped with oxidation catalytic converters, which means about 410,000-580,000 oz noble metals/year on cars plus an (estimated) additional 150,000 oz for replacement parts.

As can be seen from Table 16d, the world reserves of noble metals are sufficient to meet the projected needs for many years. Furthermore, the mining capacity in South Africa is being expanded to cover the increased demand, as shown in Table 18.[54,55] It thus appears that there will be sufficient quantities of noble metals available for the automobile applications. However, the price for these metals will undoubtedly increase, and this will cause higher prices for other products (e.g., electrical components) that also involve their use. Finally, the extended dependence on nondomestic sources for these materials is a source for concern.

As noted in Chapter 3, ruthenium has been suggested as a possible (although rather unlikely) catalyst for NO_x reduction. From Table 17 it is apparent that much less ruthenium is produced than are Pt and Pd. However, since there are no major uses for ruthenium today, significant

quantities (estimated to be in the hundreds of thousands of ounces, but exactly how much is not disclosed)[56] of the metal have been stockpiled. Also, should Ru be used in the catalysts, its high effectiveness (providing it can be stabilized) makes it necessary to use only 1/10th to 1/4th as much per car as are required for Pt and Pd.[6] Thus, from a materials supply point of view, Ru is also a possible candidate for automobile applications, and its use might help reduce the stockpile for which there is currently little demand.

TABLE 18

Growth Potential for South African Platinum and Palladium
(1000 troy oz)

	1972	1973	1974	1975
Platinum				
Rustenburg	550	900	1,300	1,500
Impala	345	400	500	650
Western Platinum	93	125	160	200
Atok	12	15	30	200
Total Platinum	1,000	1,440	1,990	2,550
Total Palladium	355	550	700	890

Source: E/MJ, March 1973

More recent figures in Ref. 57 indicate Pt will increase from 2,100,000 oz in 1974 to over 2,700,000 oz in 1975.

REFS. 54,55

Rhodium is the only other potential noble-metal candidate for use in catalytic converters. It is produced in quantities even lower than Ru (Table 17), and it is used as an alloying agent with Pt to increase its hardness, in Pt/Rh thermocouples, and with Pt as an alloy for catalytic oxidation of NH_3 to produce nitric acid. While the initial use as an exhaust-oxidation catalyst is small (and it could probably be replaced with Pd without significant problem), the material does show considerable promise for use in the three-way catalysts and also for NO_x reduction.[2] There are more potential

supply problems for Rh than for the other noble metals, and this will probably limit its use in catalytic converters to that of a minor component.

In some cases it may be possible to regenerate noble-metal catalysts that have been poisoned by lead.[4,11] The techniques suggested involve flowing through the converters a chemical solution that will specifically dissolve the lead compounds but that will not dissolve the catalyst or converter housing. Most of the lead can be removed and the catalytic activity significantly increased by this process. However, as currently formulated, the technique would involve removing the converter from the automobile for regeneration. Only laboratory tests have been conducted to date; the process has not been field tested.

In summary, supplies of Pt and Pd, although not available domestically, appear to be adequate to meet the needs of catalytic converters for the next several years. The same is true of Ru, should it be used in small quantities. With Rh there are potential supply problems, and this metal will probably not be extensively used.

Base metals - As explained in the preceding chapter, base-metal catalysts (whether reduced or oxidized) are very susceptible to poisoning at low temperatures by sulfur in the fuel. If the fuel sulfur level could be substantially decreased, there is a good possibility that these materials could be effectively substituted for noble metals, at least for limited mileages.

Among the primary contenders are Cu, Co, Ni, and Cr. It is estimated that the catalysts would require no more than two-to-three pounds of any single one of these metals, which could mean between 20 and 35 million pounds/year at most. Gould[19] has estimated that 28.8 and 32.2 million pounds (for two different formulations) of Ni per year would be required if all new cars in the U.S. were to be equipped with their NO_x catalysts. According to their figures, this would amount to 5.8-6.5% of the total Ni currently consumed in the U.S.

The consumption figures in Table 19[26] indicate that only for Ni and Co does there appear to be a potential materials supply problem.

TABLE 19

Estimated U.S. Consumption of Selected Base Metals, 1971

Metal	Millions of Pounds/year
Copper[a]	5906
Nickel	260
Chromium[a]	2300
Manganese	4000
Cobalt	11
Vanadium	9
Tungsten	800
Rare earths (as R_2O_3)[b]	12

[a] Figures include both scrap and primary; all others represent primary metal use only.

[b] Harris and Hannay, 1970, ref. 58; all other figures from Mineral Facts - 1971.

REF. 26

At present, automobiles contain about three pounds of Ni/car, most of that being utilized in construction of bumpers. Actually, the concern about base-metal shortages stems not from use in exhaust catalysts per se, but from use in the catalyst containers. Ford[2] has expressed concern about the availability of 409 stainless steel and Inconel wire used in the converters.

A few years ago there was some optimism expressed concerning the potential of perovskite-type materials containing rare earth metals as possible substitutes for noble metals.[57] At a level of 1 lb/car, such usage would equal the total use now observed.[58] This could again present supply problems. Tests to date have not shown acceptable performance of such materials.

In summary, use of base metals as catalysts in automobiles will probably not increase the consumption of any one metal by more than 10%, and increased production could probably easily handle the new demands. However, their use in construction of high temperature-resistant catalyst containers is a more serious problem.

Supports - The active-metal, automobile-exhaust catalysts are dispersed on oxide supports in the form of pellets (cylindrical or spherical) or honeycomb-shaped monoliths. The pellets are mainly gamma alumina that may contain a "stabilizer" such as MgO, CeO_2, and Na_2O.[59] In order to avoid having to certify too many different types of catalysts, the automobile companies (mainly General Motors) have made these catalysts as similar as possible, even though they are produced by different companies. The chemical and physical properties of alumina depend quite strongly on the method of preparation. The physical strength, pore-size distribution, density, level of impurities, etc. are all important parameters for the automobile application, and they can vary markedly from one manufacturer to another. At present, the most popular source of alumina for automobile catalysts is Rhone-Progil, a French manufacturer.

The ceramic monoliths, on the other hand, are all made by domestic manufacturers (Corning and American Lava), and they are mainly

cordierite (see Table 2) either extruded or preformed in a paper binder that is subsequently burned away. The channel walls of the monoliths are then coated with a high surface area gamma-alumina wash coat (about 10-20 wt%) upon which the active metals are dispersed.

The alumina used in this application will represent only a small fraction (much less than 1%) of the total material used in the U.S. today (about 8 million tons).[60] The stabilizer technology still is proprietary, but neither the stabilizer nor the alumina should pose a materials-supply problem. However, the price will probably increase due to the recent increased cost of imported bauxite from which alumina is prepared.

While materials are readily available for the monoliths, this is a relatively new technology. Each of the monolith vendors is in the process of completing (or has already completed) the necessary plants to meet the contractual obligations in this area.

Other support materials that have been suggested (either singly or in mixture) are titania, zirconia, thoria, zinc oxide, magnesia, silica, silicon nitride, etc., but none of these materials is being seriously considered at the present.

B. Toxicology

Debris from catalysts - Loss of catalytic material from the automobile converters can be attributed either to physical removal through attrition or to chemical processes by forming a compound with sufficiently high vapor pressure that it can be volatilized.

Ford data[2] with monolith catalysts indicate that within experimental error there is no measurable loss of noble metal, wash coat, or ceramic substrated under normal operating conditions. With pelleted catalysts there is slightly more material loss (presumably due to attrition), but even here the amounts are exceedingly small. Using radioactive techniques to increase analytical sensitivity, General Motors[61] was able to show that at speeds less than 30 mph with stops, the catalyst was lost at a rate of 2-3 mg/mi, but the noble metals

were displaced at a rate of only 1-2 ug/mi. Steady-state measurements at 60 mph were slightly higher, the corresponding numbers being 5 mg/mi and 3 ug/mi. Since the catalyst contained 0.06 wt% Pt, the ratio of Pt loss to total catalyst loss ($\sim$ 0.0006) indicated that both were being lost at the same rate and that the noble metal was not being lost preferentially. This amounts to less than 10% weight loss for 50,000 miles, although the volume loss may run as high as 15% due to shrinkage. Actually, these attrition tests were conducted on "fresh" catalysts with the results extrapolated to 50,000 miles. The true particulate emission may be less than these values, because the catalyst would be expected to have more attrition when new than after "aging." On the other hand, an "aged" catalyst may have a larger void volume and thus experience more movement of the particle than would occur with a "fresh" catalyst. Recent tests by Exxon[62] (although with much less sensitive analytical methods) and EPA[63] produced numbers of the same order of magnitude as those obtained by GM.

Concern has also been expressed about the chemical and physical properties of these attrited particles. Using a condensation nuclei counter, Balgord[64] detected an increase in particulate matter in the size range of 0.001 to 0.1 micron from the effluent streams of several base-metal catalysts "containing Cr, Ni, and Cu under conditions of temperature and gas composition similar to those of catalytic automotive emissions-control systems." Particles of this size are in the respirable range and could possibly have physiological activity in the lungs. No tests were reported with noble-metal catalysts, however. In their tests with radioactive isotopic tracers, General Motors[61] showed that no measurable fraction of the noble-metal particulate matter collected from automobile emissions was soluble in water, ethanol, carbon tetrachloride, or in hydrochloric acid, which clearly demonstrated that no soluble Pt compounds were in the debris. Since it is only the soluble platinum salts, and not the metal or its oxides, that show physiological activity and are responsible for such conditions as platinosis,[54,65,66] this finding is quite significant.

Palladium is considered to be less toxic than platinum in this regard.[54] Another significant point is that of the particulate matter collected in the General Motors test, 80% was larger than 125 microns (much too large to be respired). The Pt particles were probably still deposited on alumina-dust particles as the two left the converter together. The alumina should also not have any adverse physiological effects.

In a study[67] of workers in an American Cyanamid Company refinery who handled catalytic material and were exposed to dust containing Pt near the threshold limit (2 ug/m^3), no evidence was found for platinosis or other disease that could be attributed to Pt after 10 years' exposure. These levels are significantly above any that could possibly occur due to particulate matter from automobiles, and it is thus concluded that airborne Pt particles emitted from automobile catalytic converters do not constitute a potential health problem.

Another potential problem involves the fate of Pt emitted from converters and possibly deposited along roadways, or Pt left to decay in junked automobiles. There is no evidence that Pt metal can be solubilized by microorganisms, but this subject has apparently not been thoroughly investigated. In fact, Wood[68] has predicted that Pt and Pd can probably be methylated by microorganisms in much the same way as mercury is methylated,[69] but this has not been demonstrated at the present. If this did occur, there is the possibility that the Pt could contaminate water supplies and become incorporated into the human food cycle. While the small amounts of material involved make the probability of such creating a problem quite remote, studies should be carried out to determine if there exist strains of highly specific microorganisms that can accomplish Pt solubilization.

In addition to physical attrition, volatile species can be formed by reaction of catalyst components with exhaust gases. Examples are the formation of carbonyls (e.g., $Ni(CO)_4$) or oxides (e.g., RuO_4) that have significant vapor pressures and are quite toxic.[70] Fortunately, most of these species decompose at high temperatures that would normally be found in the converters, but during warm-up

and cool-down the converters will pass through a transient temperature range where such formation could occur. While this presumably accounts for the instability of Ru catalysts to oxidizing atmospheres, the Panel members are not aware of any evidence for carbonyl formation in catalytic converters.

Table 20[70] lists several compounds of potential catalytic materials and their associated toxicities. However, the small quantities of these materials that escape from the converters[62] make the potential for hazards in this area fairly remote.

It is therefore concluded that debris from catalytic converters should not represent a potential health hazard.

Effect on fuel components - The effect the oxidation catalysts have on the various fuel components will be discussed separately.

1. Phenols, polynuclear aromatics, aldehydes. Gasoline normally contains small quantities of polynuclear aromatics,[71] some of which have been identified as being carcinogenic. As larger fractions of aromatics are used for octane enhancement, more of these compounds will be present in the fuels. Since not all the fuel is burned in the engine, some of these compounds will be emitted from the vehicle, and the measured amounts have been shown to be proportional to the amount present in the fuel. Also, certain partial oxidation products (e.g., phenols and aldehydes)[71] have also been identified in the exhaust gases; such compounds are eye irritants and contribute to smog formation. Oxidation catalysts are extremely effective for removing all these compounds, their levels being reduced by more than 98%.[2,25,71]

2. Particulate matter. Numerous tests have shown that particulates from the exhausts of unregulated automobiles are due mainly to the presence

TABLE 20

Toxicity of Some Compounds That Might Be Used in Automobile Emission Control Catalysts

Compound	Acute Local	Acute Systemic	Chronic Local	Chronic Systemic	Maximum Allowable Concentration in Air (mg/M^3)
Lead compounds	0	3	0	3	0.15
Chromium compounds	3	U	3	3	0.1
Nickel compounds	1	1	2	2	0.5
Nickel carbonyl	3	3	1	3	
Manganese compounds	U	2	U	3	15.0
Copper compounds	1	2	1	1	
Metal carbonyls	3	3	U	3	
Alumina	1	0	2	0	
Silica	2	0	3	1	
Cobalt compounds	1	1	1	1	0.5
Tungsten compounds	U	1	U	1	
Magnesium compounds	1	2	2	0	15.0
Ruthenium compounds	(Details unknown, but probably toxic)				0.01
Ruthenium tetroxide	2	U	U	U	
Platinum compounds	(very low toxicity)				
Palladium compounds	(very low toxicity)				
Mercury					0.1

Source: Sax, 1963 (reference 70)

Note: 3 very toxic
2 moderately toxic
1 slightly toxic
0 nontoxic
U unknown toxicity

REFS. 26, 70

of lead in the fuel.[2,25,62] Removal of lead motor mix causes a reduction by over a factor of 10 in particulate matter.[2,25] However, a small increase (over the lead-free case) occurs in emission of particulate matter when an oxidation catalyst is present (using unleaded gasoline), but this is still far below the leaded gasoline-no catalyst case. The increase is due mainly to sulfate formation, as discussed in the next section. Overall, particulate emission will be considerably reduced with the use of catalytic converters with unleaded gasoline.

3. Sulfate emission. Sulfur normally present in fuels (about 0.03 wt%) is emitted from engines mainly as SO_2, which is slowly oxidized (depending on atmospheric conditions) in the air to SO_3. This gas reacts with water to form sulfuric acid aerosols that can react with airborne ammonia (or other basic compounds) to produce particulate sulfates, compounds that may have adverse physiological effects if breathed. Oxidation-catalytic converters cause a part of the SO_2 to be oxidized to SO_3 before it leaves the car, and concern has been expressed that this may result in dangerously high sulfate levels near freeways even though sulfur in gasoline represents less than 1% of all sulfur emitted into the atmosphere by man-made sources in the U.S.[72]

Catalysts that are active for HC and CO oxidation also oxidize SO_2 to SO_3. (It may be of interest to note that the first patent in catalysis involved use of Pt for SO_2 oxidation in the "contact process" for sulfuric acid manufacture.)[73] The percentage of SO_2 that can theoretically be converted depends on the temperature and oxygen

partial pressure, as shown in Figure 25.[4] Lower temperatures and higher oxygen concentrations favor the oxidation. Furthermore, the catalysts (depending on type, whether pelleted or monolithic) have a capacity to retain (or "store") considerable quantities of sulfur compounds,[72] particularly at low temperatures, and this material is subsequently desorbed (or "dumped") from the catalyst at elevated temperatures. These factors, coupled with some uncertainties about the reliability of analytical procedures for sulfur compounds, make it impossible to predict exactly how much SO_3 will be formed without considerable knowledge about the system parameters and the catalyst's prior exposure to sulfur.

Data from Ford[2] and General Motors[72] indicate that there is almost no SO_3 emitted from the engine, although Chrysler[38] and EPA have shown that up to 15% of the sulfur is emitted as SO_3. In any case, the oxidation of SO_2 is not very high in the absence of a catalyst, even with air injection into the manifold. In oxidation catalyst-equipped cars, the oxidation figures range from only a slight enhancement[72] to 84%[2] conversion (based on the SO_3/SO_2 ratio in the tailpipe and disregarding any storage effects). In most cases the conversion achieved is in the range of 10-25% without air injection to 30-60% with air injection. Usually the observed conversions are well below the thermodynamic equilibrium values, as seen in the Ford data

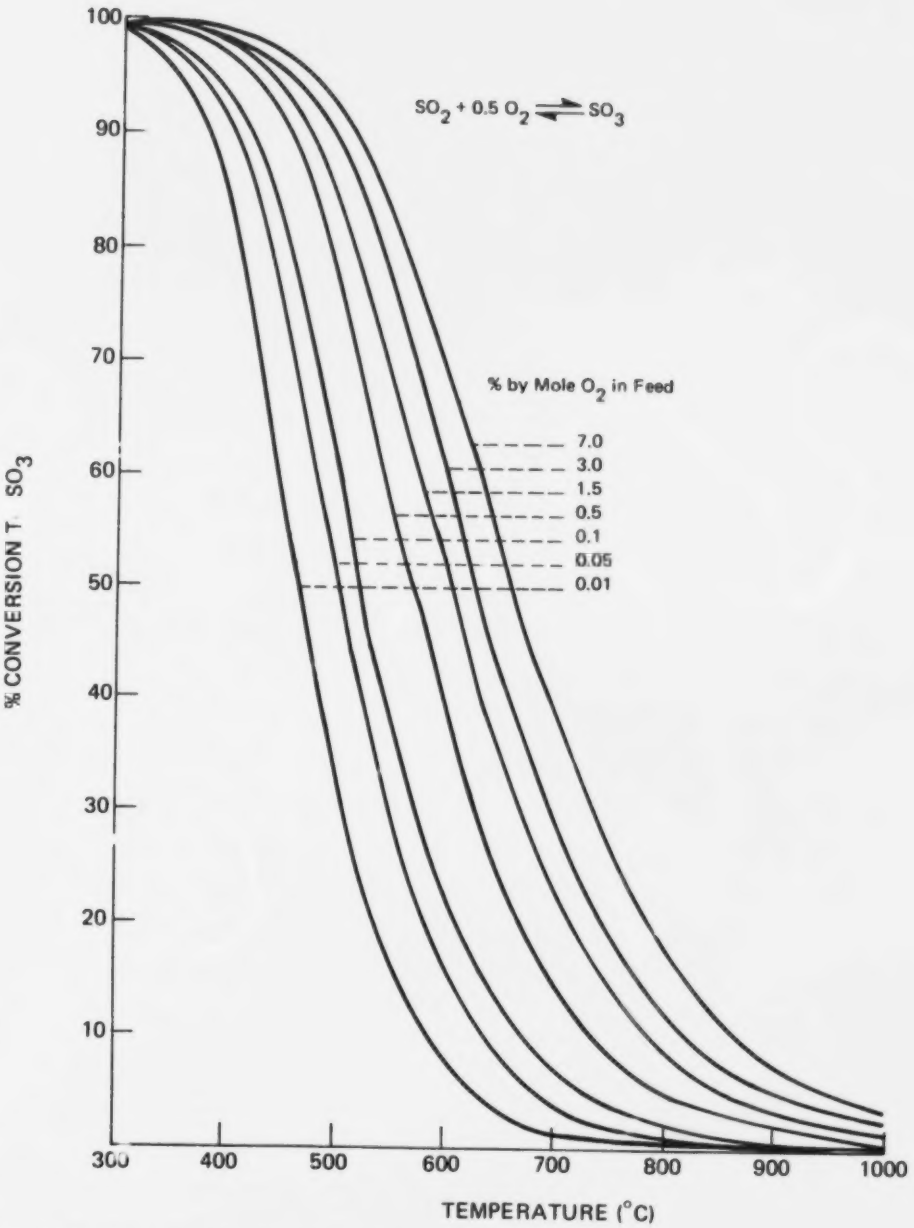

FIGURE 25 Equilibrium Conversion of SO_2 to SO_3 at 1 atm Pressure.

REF. 4

in Figure 26.[2] The fractional conversion is generally independent of fuel sulfur content, although the fractional conversion decreases as most catalysts are aged. There is much less storage of sulfur on monolithic catalysts than on the pelleted forms. The larger amount of alumina in the pellets makes this result not unexpected if the sulfur is held as $Al_2(SO_4)_3$ which decomposes at high temperature to release SO_3.

Neglecting any storage effects and assuming a car gets 15 mpg on fuel with 0.03% by weight S, about 0.07 g S will pass through the engine per mile. If all this S were burned to SO_2 in the engine, oxidized to SO_3 in the catalytic converter, and transformed into sulfuric acid (H_2SO_4) before leaving the tailpipe, then this would amount to about 0.2 g H_2SO_4/mi. In view of the partial conversion that actually occurs in the converter, it seems reasonable to assume that on the average there would be about 0.05 g sulfur compounds (calculated as H_2SO_4) emitted per mile under steady state conditions (i.e., after the catalyst has become saturated with sulfur under the conditions used for the test).

The 1972 Federal Test Procedure (CVS-C, which involves only the "cold start" portion of the cycle) cannot be used as a reliable measure of the total SO_3 (or H_2SO_4 or sulfate) emissions because of the sulfur storage problem. As may be seen in the GM data in Figure 27,[25] measured sulfur emissions for 0.03% S fuel fall between 0.001 and 0.020 g/mi for various converter types and operational modes; these values are considerably lower than the steady state value.

Several modeling studies have attempted to predict the concentration of sulfates that might be expected from various assumptions and meteorological conditions. The most popular approach has been to assume that sulfates

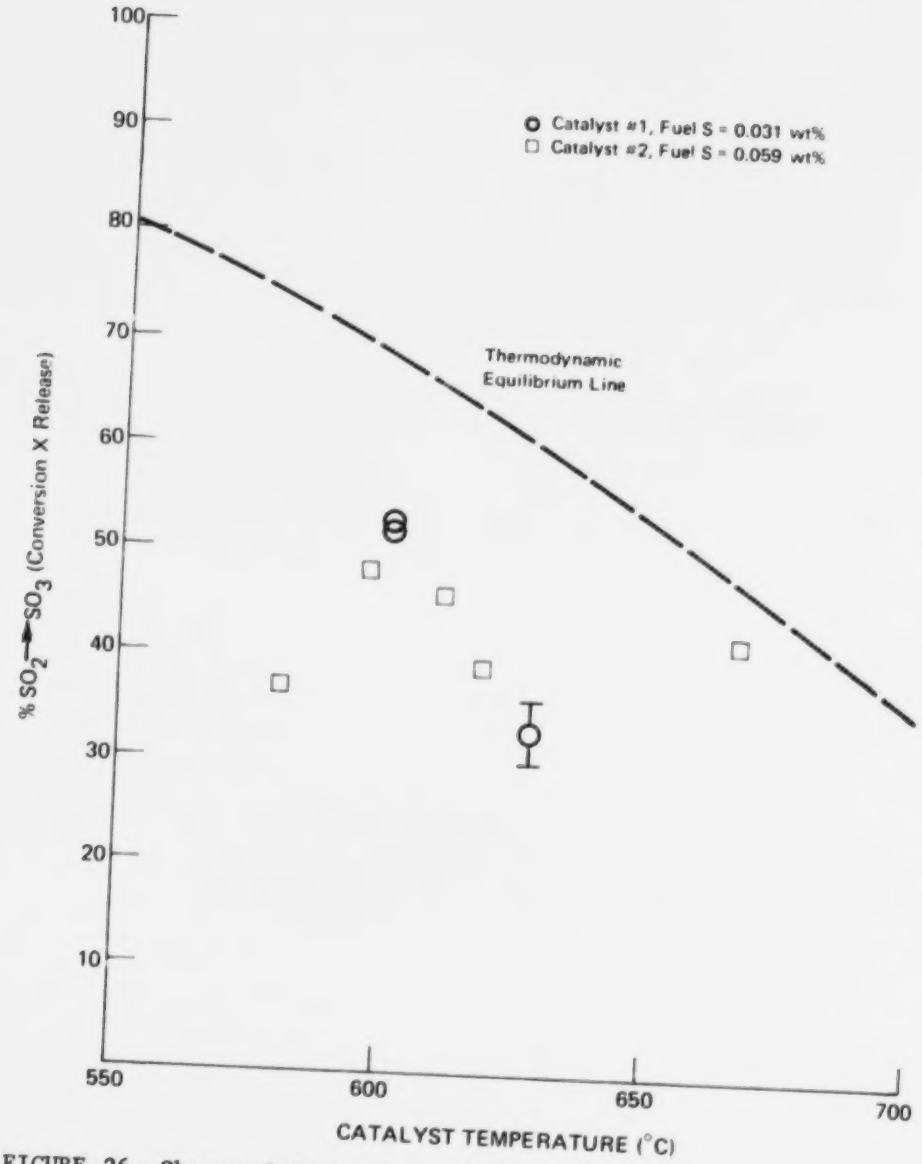

FIGURE 26 Observed Conversion of SO_2 to SO_3 Compared with Thermodynamic Equilibrium Curve for SO_2 to SO_3.

REF. 2

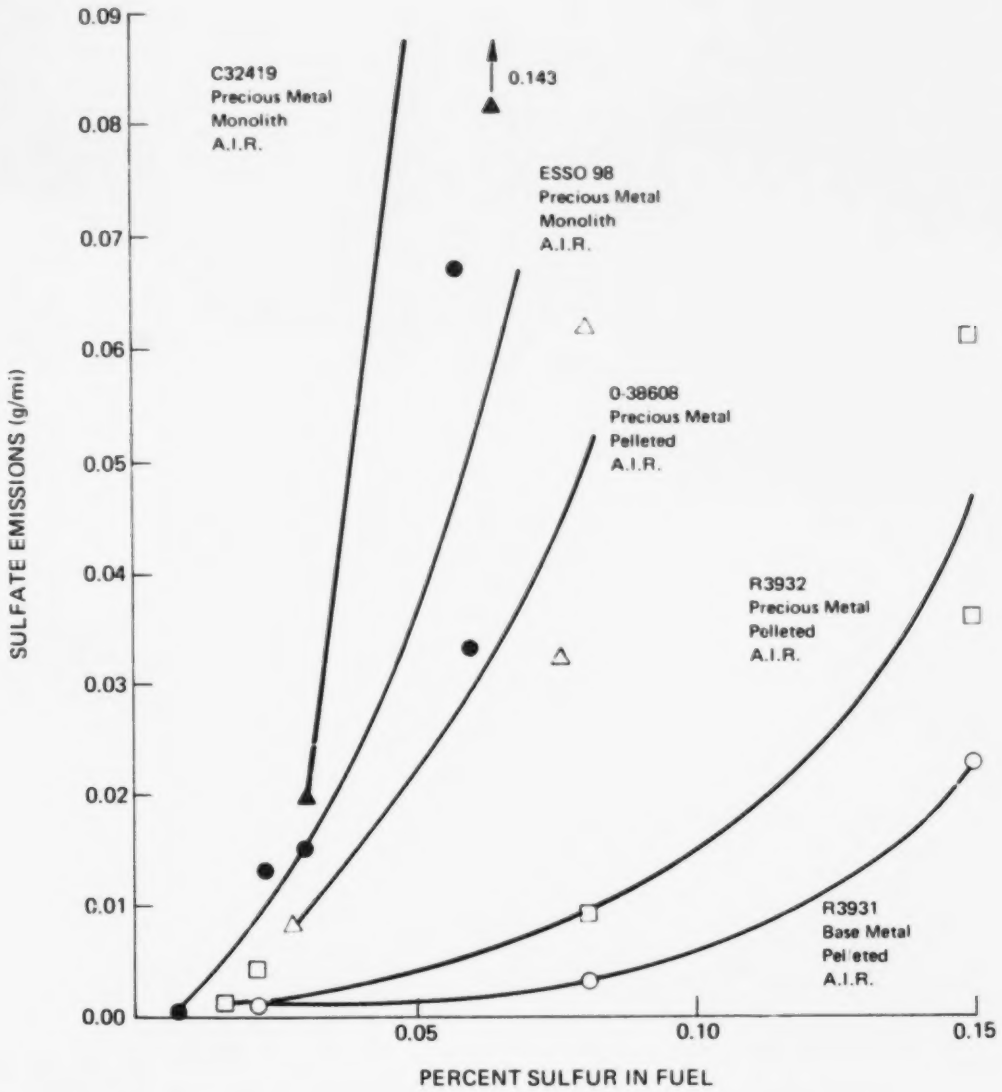

FIGURE 27 Effect of Fuel Sulfur Content on Sulfate Emissions, 1972 Federal Test Procedure.

REF. 25

will be transported through the air near motorways in much the same way as more stable automobile exhaust pollutants (e.g., CO or Pb) for which concentration profiles are available. Mathematical models (called "surrogate" models) that adequately describe these known concentrations can then be modified and applied to predict the behavior of sulfates. A second surrogate estimate is based on the observed carboxyhemoglobin levels (which are related to atmospheric CO levels) in healthy blood donors from 18 cities in the U.S. By assuming that all or most of the CO exposure is due to emissions from automobiles and that a relationship between CO and sulfate emissions can be established, it is possible to provide another estimate of sulfate exposure that might be expected. In all models, both typical and adverse meteorological conditions were assumed, and sulfate concentrations were than predicted for roadside and nearby locations. Some of the results are summarized in Table 21,[72a] which has been based on only two model years (or 25% of the vehicle-miles driven) with cars having catalytic converters. The GM data, based on measured SO_3 emissions under non-steady state conditions where sulfur retention is significant, showed 24-hour exposure values from 0.7 to 3.6 ug/m^3 at roadside to 0.4-2.1 ug/m^3 10 meters from the road. Actually, these values should all be multiplied by a factor of 8 to be applicable under steady state conditions, which brings the predicted sulfate concentrations into the range of 3 to 30 ug/m^3 under adverse conditions. These numbers are similar to predictions of other models shown in Table 21. Under very adverse atmospheric conditions, the various models predict peak concentrations could go as high as 124 ug/m^3. Even though such a

TABLE 21

Modeling Studies of Sulfate Concentrations

Maximum 24-hour Sulfate Exposures

(Based on 25% of vehicle-miles on catalyst-equipped cars)

Investigator	Estimation Method	Atm. Condition	Assumed Emissions (ug/mile)	H_2SO_4 Conc., ug/m^3 Roadside	10 Meters Away
GM	Gaussian				
	90° Wind	Adverse	0.007	0.9*	0.7*
	Max angle	Adverse	0.007	3.6(3°)*	2.1(5°)*
GM	St. Canyon				
	Expr.	Adverse	0.007	1.6*	0.8*
	Art. Hwy.	Adverse	0.007	0.8*	0.4*
GM	Pb tracer	---	0.007	0.7*	0.4*
GM	CO tracer	---	0.007	---	0.7*
Ford	Pb Surrogate	Adverse	---	5.0	---
EPA	CO Dispersion	Adverse	0.05	14.5**	11.1**
EPA	CAMP Station	Max. CO	0.05	5.3	
EPA	Pb Surrogate	---	0.05	1.7-9.2	
EPA	COHb	---	0.05	1.0-8.1	

*Numbers should be mutiplied by 8 due to low assumed SO_3 emission rate

**Could be as high at 124 and 88 for peak adverse conditions

REFS. 72, 72a

concentration would only be expected to occur rarely (if at all), its possibility must be considered in light of documented adverse health effects these compounds may have on a significant fraction of the population who may be particularly sensitive. The EPA, in its "CHESS" Studies,[72b] has concluded that sulfate (or, more specifically sulfuric acid) concentrations in the range as low as 8-10 ug/m^3 can aggravate symptoms of asthmatics and people with cardiopulmonary diseases. Furthermore, it is not only the mass concentrations but also the chemical composition and physical state of the various compounds that are important.[72c] For example, sulfuric acid is much more toxic than ammonium sulfate, and particle sizes in the respirable range (less than 1μm in diameter) do more damage than larger particles.

It should be kept in mind that all SO_2 emitted into the atmosphere (less than 1% actually comes from automobiles) is eventually converted to sulfates with the rate of conversion depending strongly on the atmospheric conditions. Thus, the overall sulfate loading in the atmosphere will not be altered by the introduction of catalytic converters. However, the SO_3-H_2SO_4-sulfate concentrations near motorways will almost certainly be increased by use of catalytic converters, and in some cases, these increases may be substantial. It is therefore extremely important that carefully planned tests be initiated to monitor the sulfate concentrations in areas where harmful levels may develop, such as in downtown street canyons, near arterial

freeways, or in shopping centers. If the sulfate concentrations approach harmful levels, then steps should be taken to reduce the sulfur content in fuels and/or modify (or eliminate) converters in order to avoid street-level formation of SO_3.

In practice, the problem may not be quite so bad as the numbers in Table 21 indicate. As mentioned earlier in this section, the SO_2 to SO_3 conversion activity decreases considerably as the catalysts age, and this would lower the predicted sulfate concentrations. Furthermore, the additional refining needed to produce lead-free gasoline will reduce the sulfur content and thus lower the overall sulfur output.[35] On the other hand, "dumping" of the accumulated sulfur in congested areas could even intensify the problem, but this is not very likely to be the case.

4. Other pollutants. There have been reports that under a very limited set of conditions (slightly reducing atmosphere, such as may occur during downhill coast), H_2S is produced. This was first noticed by Chrysler personnel who smelled the gas. While the levels are well below those that represent a health hazard, the odor could be a mild annoyance. Also, with high phosphorous contents there is the possibility of producing highly toxic phosphine,[38] but the current phosphorous levels are much too low to form a basis for concern.

Neither ammonia nor nitrous-oxide (N_2O) emissions will occur with oxidation catalysts. Besides, both are present in the atmosphere at levels far above those that would be emitted from cars, so neither appears to present a significant addition to current pollutant levels.

Animal tests - To examine directly the health effects of exhaust catalyst-equipped cars, several experiments[74] were carried out with Sprague-Dawley rats in special chambers through which diluted exhaust could be passed. Animals subjected to the catalyst equipped exhaust could not be distinguished from those breathing purified air, while animals subjected to noncatalyst exhaust fared much worse. In the preliminary draft of their report, the experimenters made this statement:

> It can be concluded that the introduction of catalytic converters into the automobile exhaust system not only has reduced the levels of certain exhaust constituents but has effectively decreased or eliminated (harmful)* biological effects studied.[74]

However, the conclusions of this report have been challenged because of the type of animals used in the study. Treon et al.[74a] have shown that rats are not very sensitive to exposure to sulfuric acid; in fact, animals follow the increasing sensitivity order

$$\text{rabbits} < \text{rats} < \text{mice} < \text{guinea pigs.}$$

Hence, a more significant test would have been to use guinea pigs, who have been shown to die of sulfuric acid exposures not lethal for the other species.[72c] The most significant test, of course, would involve human subjects, but ethical constraints prevent extensive tests of this kind.

Despite this criticism, it does seem that, except for possible problems arising from sulfuric acid emissions, catalytic converters will have a substantial impact on improving the quality of air in the vicinity of motorways.

*(harmful) added by the members of the Panel of Consultants on Catalysts

VI. KINETICS, MECHANISMS, AND MODELING

A. Introduction

Information on kinetics and mechanism, and reaction and reactor models developed from that information, are normally the product of extensive basic research programs. While considerable information is available concerning the kinetics and mechanisms of oxidation reactions of HC and CO on the noble metals to be employed as emission-control catalysts, very little of it is applicable to the conditions peculiar to these devices. Thus, much of the development work on catalytic devices for automobile emissions control has been done in terms of prototype experiments with rather meager knowledge of the chemical fundamentals.

Fortunately, under most operating conditions, exhaust converters are transport limited, which means the rates of mass and heat transfer to and from the catalytic surface, rather than the intrinsic chemical kinetics, determine the conversion to products. Given this situation, one would think that reactor modeling would be a fruitful area for work; in fact, relatively little effort has been expended in this direction to date. This is due primarily to the difficulty in reactor analysis of the major catalyst problem, that of long-term durability.

This chapter contains a summary of pertinent information on the kinetics of CO and HC oxidation and NO_x reduction, together with a report on the current state of exhaust converter modeling.

B. CO Oxidation

To a first approximation, the kinetics of CO oxidation under typical automotive exhaust environments can be represented by the following rate equations:[75]

$$\frac{d(CO)}{dt} = -k_1(CO)^{0.7} \qquad \text{(base metals)}$$

$$\frac{d(CO)}{dt} = -k_2(O_2)/(CO) \qquad \text{(platinum)}$$

In both cases the rate constants k_1 and k_2 are sensitive to the levels of water and of hydrocarbons in the reaction mixture, reflecting an adsorption competition among these species on the catalyst surface. Carbon monoxide is more strongly adsorbed on transition metal surfaces, hence the adsorption inhibition noted above for platinum would be expected to pertain to Pt/Pd formulations as well. At very low CO levels, the inhibition has been reported to disappear and the rate to depend on a positive order for CO.[76] In general, rate correlations of the form

$$\frac{d(CO)}{dt} = -k(CO)^x(O_2)^y$$

have been found successful for a number of transition metals. Some typical values are[77]

Material	x	y	Temperature (^oC)
Pd wire	-2	1	100
Pd foil	-1	1	300
Pt wire	-1	1	---
Ag foil	1	1	450

While no experimental information has been found which would permit the unequivocal modeling of the adsorption competition between CO, H_2O, HC and O_2, it is not unreasonable to expect that a Langmuir-Hinshelwood correlation could be developed. This would have the form

$$\frac{d(CO)}{dt} = -k \frac{K_{CO}K_{O_2}(CO)\ (O_2)}{(1 + K_{O_2}(O_2) + K_{CO}(CO) + K_w(H_2O) + K_{HC}(HC))^2}$$

where the K values are adsorption equilibrium constants. For strong chemisorption of CO, this form is also compatible with the power law forms given above.

Conventional interpretation of the mechanism of CO oxidation on transition metals, based on this kinetic information, suggests reaction between chemisorbed oxygen and CO, with the active surface mostly occupied with CO. Recent work, however, indicates that the mechanism

at low CO levels is at least partially controlled by a parallel reaction of gaseous CO with adsorbed oxygen atoms.[78] On some base-metal oxides, especially in those cases where lattice oxygen mobility is high, the oxidation mechanism involves an oxidation-reduction cycle of the catalyst, with the active oxygen supplied by the catalyst and a possible carbonate intermediate. A thorough review of mechanistic studies on base-metal oxides is available.[79]

C. HC Oxidation

While CO is more difficult to oxidize than HC in an homogeneous thermal reactor, it is the latter that is most demanding in a catalytic system. Hydrocarbon oxidation can be conveniently divided into two parts: oxidation of saturated materials and oxidation of all other types. Aromatics, olefins, partially oxidized products such as aldehydes and ketones, are all easily converted to CO_2 and water over most catalysts under mild conditions. However, paraffins behave quite differently, the ease of oxidation decreasing as the chain length becomes less. Except under very harsh conditions, methane is hardly affected by oxidation catalysts. When catalysts become slightly poisoned, it is almost always the hydrocarbon conversion that first begins to decrease.

Little information is available about the mechanisms of these extremely complex reactions. Partially oxidized surface species are undoubtedly involved, but none of these species has been observed in the exhaust streams after the catalysts. This indicates that once formed they must be quite rapidly oxidized completely.

D. NO_x Reduction

Unlike the case for CO and HC oxidation, with their long history in the literature, the catalytic reduction of NO_x has been studied most extensively by those with an interest in automobile emission control. A general review of the behavior of NO in heterogeneous

catalytic reactions leading to reduction of the NO has been given by Shelef and Kummer.[80] In applications to emission control, the reduction of NO (considered as an overall process) is very complex due to the variety of reactions involved, such as

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

$$2CO + 2NO \longrightarrow N_2 + 2CO_2$$

$$5H_2 + 2NO \longrightarrow 2NH_3 + 2H_2O$$

$$2NH_3 \longrightarrow N_2 + 3H_2$$

$$4NH_3 + 6NO \longrightarrow 5N_2 + 6H_2O$$

$$2H_2 + 2NO \longrightarrow N_2 + 2H_2O$$

The importance of the water-gas shift (first reaction) in supplying hydrogen for reduction and the role of NH_3 in the overall reduction are now well recognized and the subject of considerable current research.

The overall kinetics of the reaction sequence outlined above have not been studied in detail, either on noble- or base-metal catalysts; however, some of the industrial reactions have been investigated. Kinetic models have been proposed by Peters and co-workers[81-83] for reduction of NO with H_2, CO and CH_4 (reduction to N_2), and for reduction with H_2 to NH_3, all over various base-metal catalyst formulations containing Cu, Zn, Cr_2O_3, etc. In the former case, the rate is correlated by

$$\frac{d(NO)}{dt} = -k_1 \frac{K_{NO} K_R P_{NO} P_R}{(1 + K_{NO} P_{NO} + K_R P_R)^2}$$

where R is either H_2, CO, or CH_4. For the reduction to NH_3 by H_2

$$\frac{d(NO)}{dt} = -k_2 \frac{K_{H_2} P_{H_2}}{(1 + K_{NO} P_{NO} + K_{H_2} P_{H_2})}$$

Some values of the rate and adsorption parameters for these models are given in Table 22a. Though determined for a particular base-metal

TABLE 22a

Parameters for NO Reduction to N_2 by H_2 on a Cu-Zn-Cr_2O_3 Catalyst (Girdler)

$k_1 = 1.39 \exp(-10{,}300/RT)$ g moles/min g

$K_{NO} = 3.1 \times 10^5 \exp(-13{,}300/RT)$ atm^{-1}

$K_{H_2} = 4.5 \times 10^5 \exp(-15{,}460/RT)$ atm^{-1}

Parameters for NO Reduction to NH_3 by H_2 on a Cu-Zn-Cr_2O_3 Catalyst (Girdler)

T, °C	$k_2 \times 10^4$, g moles/min g	K_{NO}, atm^{-1}	K_{H_2}, atm^{-1}
375	0.77	6.17	16.41
400	2.13	10.32	13.49
425	2.78	11.71	21.6

Note: These parameters do not fit an exponential temperature relationship, as did the parameters for reduction to N_2.

REF. 81

formulation, they are probably good as order-of-magnitude estimates for related base-metal formulations. The parameters for ammonia formation vary irregularly with temperature and thus have empirical significance only.

More recently London and Bell[84] have reported the kinetics of NO reduction with CO on silica-supported copper oxide. They obtained a kinetic correlation of the form

$$\frac{d(NO)}{dt} = - \frac{2b_1 b_2 C_{NO}}{(1 + b_2 C_{NO} + b_3 C_{N_2O})\ (1 + b_4 C_{CO})}$$

The equation is consistent on a mechanism involving dissociative adsorption of NO, N_2O acting as intermediate in N_2 formation, and CO maintaining the surface in a reduced state as well as competing for the sites required for NO dissociation. Typical values of the constants in the rate equation are given in Table 22b.

Of special interest is the formation of an isocyanate surface intermediate (NCO) during the reduction of NO by CO. That such a surface intermediate is detectable both on noble-metal catalysts[85,86] (Pt, PD, Rh, Ir, Ru) and on a base-metal catalyst[84] (Cu) suggests an interesting interpretation of the mechanism of NO reduction and of ammonia formation. The existence of an isocyanate surface structure as detected by infrared spectroscopy under reaction conditions points to dissociative chemisorption of NO as an essential step in this reaction.

As for the question of NH_3 formation, either by reduction of the nitrogen adatoms with hydrogen species or by hydrolysis of the isocyanate adsorbate, the studies by Unland[85] tend to favor the latter mechanism. On noble-metal surfaces he reports that the tendency for ammonia formation is related to the (NCO)-forming properties of the respective metal. In the case of ruthenium, this surface species exhibits a very low surface density as compared with the other metals studied.

Table 22b

Parameters for NO Reduction to N_2 by CO on Silica-Supported Copper Oxide

T °C	b_1	b_2	b_3	b_4
135	0.011	2403	0	4392
170	0.023	2942	0	2103
200	0.012	2137	0	2098

REF. 84

A most recent study of the reduction of NO by H_2 and/or CO over noble-metal catalysts has indicated a marked difference between the behavior of Pt and Pd on the one hand and Rh and Ru on the other. While the reaction of NO with H_2 predominates in each of the cases studied, CO acts as an inhibitor in the case of Pt and Pd. Over Ru, however, the reaction is accelerated by CO. These observations are interpretable in terms of the isocyanate surface species acting as an ammonia precursor and reaction inhibitor, since it competes with NO and CO for surface sites involving nitrogen adatoms, viz:

$$N_s + NO \longrightarrow N_2 + O_s \qquad (a)$$

$$N_s + CO \longrightarrow NCO_s \qquad (b)$$

Reaction (a) leads to N_2 formation and CO oxidation by way of the subsequent reaction

$$O_s + CO \longrightarrow CO_2 \qquad (c)$$

On the other hand, the NCO surface species are relatively stable and unreactive under the experimental conditions, except possibly to an hydrolysis reaction with ammonia as a product.

E. NO Decomposition

The ideal way to eliminate NO from automobile exhausts (or from stack gases) is simply to decompose it, since NO is thermodynamically unstable except at very high temperatures. All that is

required is a catalyst that will somehow activate the N-O bond. If this could be realized, NO could be removed under oxidizing conditions rather than requiring a net fuel-rich (or reducing) atmosphere as seen in the preceding section. Unfortunately, no such catalyst has been found that will operate at low or moderate temperatures. Several base metals and noble metals, in their reduced state, will react quite readily with NO to form N_2; however, the oxygen remains tightly bound to the surface and oxidizes the catalyst. Once the surface is covered with O atoms, the reaction ceases and will not begin again until a reducing molecule (CO, H_2, HC, etc) chemically removes the interfering O atoms. Of course, this then becomes an example of NO reduction.

Amirhazmi, Benson, and Boudart[87] have recently reviewed NO decomposition. In general, most investigators find the reaction can be treated by a Langmuir-Hinshelwood equation with strong inhibition by adsorbed oxygen. Table 23 shows a collection of parameters for this reaction.

F. Exhaust Converter Modeling

Contacts with both automotive and catalyst manufacturers revealed, with one exception, no current activity in trying to model the behavior of exhaust converters, either fixed beds or monoliths. The single exception is General Motors, where there has been some effort in modeling deactivation effects in individual catalyst particles.[88] These consider the interrelations between chemical rates, diffusion rates, and deactivation rates in determination of the net activity of a given catalyst. They also investigated the relationship between pore structure and susceptibility to poisoning. The approach is similar to that reported previously by Masamune and Smith.[89]

The primary interest in modeling of exhaust converters seems to reside in the academic community. These efforts are largely confined to monoliths. Two papers on the topic, both including transport

TABLE 23

Summary of Catalytic NO Decomposition Kinetics

Authors	Catalyst	Reactor	Gas Mixture	Temperature range, °C	Pressure, Torr	Reaction w/ respect to NO	Ref.
Fraser and Daniels	Metal oxides	Flow	10% NO in He	740-1040	760	0	(2)
Yur'eva et al.	Transition metal oxides	Recycle	100% NO	250-750	100-380	2	(3)
Shelef et al.	Supported Pt and oxides	Flow	4-100% NO in He	279-938	760	~1	(4)
Winter	Oxides	Recycle	100% NO	330-870	50-400	1	(5)
Bachman and Taylor	Pt wire	Batch	100% NO	1210	201-479	2	(6)
Zawadski & Perlinsky	Pt-Rh wire	Batch	100% NO	860-1060	100	1	(7)
Green & Hinshelwood	Pt wire	Batch	100% NO	882-1450	200-500	1	(8)
Sakaida et al.	Supported Pt-Ni	Flow	0.404 & 0.432% NO in N_2	427-538	1-15 atm	2	(9)

References for table

2. Fraser, J.M. and Daniels, F., J. Phys. Chem., 62, 215 (1958).
3. Yur'eva, T.M., Popovskii, V.V., and Boreskov, G.K., Kinet. Katal. 6, 941 (1965).
4. Shelef, M., Otto, K., and Gandhi, H., Atm. Environ. 3, 107 (1969).
5. Winter, E.R.S., J. Catal. 22, 158 (1971).
6. Bachman, P.W., and Taylor, G.B., J. Phys. Chem. 33, 447 (1929).
7. Zawadski, J., and Perlinsky, G., Compt. Rend. 198, 260 (1934).
8. Green, T.E., and Hinshelwood, C.N., J. Chem. Sco. 129, 1709 (1926).
9. Sakaida, R.R., Rinker, R.G., Wang, Y.L. and Corcoran, W.H. AIChE J. 7, 658 (1961).

and kinetic effects and capable of describing thermal transients, are to be presented at a forthcoming Symposium on Chemical Reactor Engineering,[90,91] and a review paper summarizing the bulk of work to date will appear in "Catalysis Reviews - Science and Engineering" in the fall of 1974.[92] Apparently none of these mathematical models of monolithic converters has been tested with experimental data, nor do they include catalyst deactivation.

All the above citations to monolith modeling, however, pertain to work that is not published at the present time. There are a few efforts at modeling that have been publicly described, some of which are summarized here. Young and Finlayson[93] describe a monolith model, based on CO oxidation alone, postulating laminar flow in each duct, negligible axial diffusion or conduction, transient response controlled by thermal response of the solid, net adiabatic operation, and no internal (pore) diffusion limitation; the model equations were solved by numerical methods. Hegedus[94] has analyzed the effects of channel geometry on monolith performance, assuming the overall rate was determined by the rate of mass transfer to the catalyst surface. He found that channels of elongated rectangular cross section were preferable in their mass transfer characteristics to other geometries (i.e., hexagons, circles, squares, etc.). The preference criterion was based on the minimum length of a monolith required for a specified conversion level. However, it should be noted that, in mass-transfer limited operation, facilitated mass transfer implies facilitated poisoning as well. The implications of this have not been fully explored, although for pelleted catalysts Wei[95] has suggested that an "egg yolk" catalyst (one with the active component buried beneath the surface) may be preferable to an "egg shell" catalyst with the active component located on the external surface of the pellets.

Johnson and Chang[96] have carried similar calculations to those of Hegedus, and Carberry and Kulkarni[97] have analyzed the intra-interphase temperature gradients likely to occur under typical exhaust operating conditions. Their results indicate that very large

interphase (gas to catalytic surface) thermal gradients are possible, and these may lead to burnout. None of these models incorporate deactivation phenomena in their description of the converter system.

REFERENCES

1. Furlong, L.E., E.L. Holt, and L.S. Burnstein, "Emission control and fuel economy," a paper presented at the American Chemical Society's National Meeting in Los Angeles, April 1974.

2. Data presented to the Panel of Consultants on Catalysts by Ford, May 6, 1974.

3. Chrysler Corporation's "Application for Suspension of 1976 Motor Vehicle Standards (Part I)," to EPA, May 1973.

4. Data presented to the Panel of Consultants on Catalysts by Engelhard Industries, June 10, 1974.

5. Chrysler Corporation, Material Standard MS 5747, March 12, 1974.

6. Data presented to the Panel of Consultants on Catalysts by Gulf Research and Development, June 5, 1974.

7. Shelef, M. and H.S. Gandhi. Platinum Metals Rev. XVIII (1974), 2; Ind. Eng. Chem. Prod. Res. Dev., II, (1972), 2.

7a. Kobylinski, T.P., B.W. Taylor and J.E. Young, SAE Paper 74250, February 1974.

8. McArthur, D.P. "Activity, selectivity, and degradation of auto exhaust noble metal oxidation catalysts," paper presented at the Third No. Am. Meeting of The Catalysis Soc., San Francisco, February 1974.

9. Taylor, K.C., R.M. Sinkevich, and R.L. Klimisch, General Motors Report GMR-1538, PCP-19, February 1974.

10. Klimisch, R.L. and K.C. Taylor, "Catalytic reduction of NO over an oxygen-treated Ru catalyst," paper presented at the California Catalysis Society Meeting, Pasadena, November 1973.

11. Data presented to the Panel of Consultants on Catalysts by Union Oil Research Labs, April 2, 1974.

12. Mannion, W.A., K. Aykan, J.G. Cohn, C.E. Thompson, and J.M. Mooney, "Catalytic reduction of NO_x emissions in auto exhaust gas," paper presented at the American Chemical Society's National Meeting in Los Angeles, April 1974.

13. Data presented to the Panel of Consultants on Catalysts by American Oil Company, March 28, 1974.

14. Simpson, H.D. "Performance and durability data for Union Oil stabilized ruthenium NO_x catalysts," paper presented at American Chemical Society's National Meeting, Los Angeles, April 1974.

15. Jackson, H.R., D.P. McArthur, and H.D. Simpson, "Catalytic NO_x reduction studies," SAE Paper No. 730568, Detroit, May 1973.

16. Burnstein, L.S., R.J. Long, R.S. Lunt, G.S. Meisser, and R.J. Fedor, "Nickel-copper alloy NO_x reduction catalysts for dual catalyst systems," SAE Paper No. 730567, Detroit, May 1973.

17. Fedor, R.J., C.H. Lee, and M.P. Makowski, "Metallic catalysts," paper presented at the Am. Inst. of Chem. Engs. National Meeting, New Orleans, March 1973.

18. Lunt, R.S., L.S. Burnstein, J.G. Hansel, and E.L. Holt, SAE Paper No. 720209, 1972.

19. Data presented to the Panel of Consultants on Catalysts by Gould Inc., June 13, 1974.

20. Bentley, D.R. and D.J. Schweibold, "Questor reverter emission control system--total vehicle concept," Fuels and Lubricants Div. of Nat. Petro. Refiners Assn. Nat. Meeting, Houston, September 1973.

21. Questor Corporation Report to the National Academy of Sciences, March 20, 1974.

22. Giordano, N., E. Cavaterra, and D. Zema. J. Cat. V (1966), 325.

23. Holbrook, L. and H. Wise. J. Cat. XXVII (1972), 322.

24. Haensel, V. and M.J. Sterba, "Energy and emission control," presented to EPA, June 25, 1973.

25. Data presented to the Panel of Consultants on Catalysts by General Motors, May 7, 1974.

26. Wei, J., R.L. Burwell, J.W. Hightower, D.F. Ollis, and H. Wise, "Evaluation of Catalysts as Automotive Exhaust Treatment Devices," Catalyst Panel Report to the NAS Committee on Motor Vehicle Emissions, March 28, 1973.

27. Data presented to the Panel of Consultants on Catalysts by Volkswagenwerk AG, May 24, 1974.

28. Data presented to the Panel of Consultants on Catalysts by Corning, June 5, 1974.

29. Data presented to the Panel of Consultants on Catalysts by Nissan, May 23, 1974.

30. Data presented to the Panel of Consults on Catalysts by Saab, May 23, 1974.

31. Data presented to the Panel of Consultants on Catalysts by Exxon Research and Engineering, June 3, 1974.

32. Data presented to the Panel of Consultants on Catalysts by Houdry Division, Air Products and Chemicals, June 6, 1974.

33. Data received from General Motors, private communication.

34. McConnell, R.J. and J.F. McDonnell, SAE Paper No. 730597, 1973; Bouffard and Waddey, SAE Paper No. 740135, 1974.

35. Data presented to the Panel of Consultants on Catalysts by Universal Oil Produces Company, May 16, 1974.

36. Gagliardi, J.C., C.S. Smith, and E.E. Weaver, API Meeting, Div. of Refining, New York, May 1972.

37. Hofer, L.J.E., J.F. Schultz, and J.J. Feenan, Bureau of Mines Report No. RI-6243, 1963.

38. Data presented to the Panel of Consultants on Catalysts by Chrysler Corporation, May 6, 1974.

39. Giacommazzi, R.A. and M.F. Holmfeld, "The effect of lead, phosphorus, and sulfur on deterioration of two oxidizing bead-type catalysts," SAE Paper No. 730595, May 1973.

40. Klimisch, R.L., J.C. Summers, and J.C. Schlatter, "The chemistry of degradation in automobile emissions control catalysts," GMR-1539, paper presented at Third No. Am Meeting of The Catalysis Society, San Francisco, February 1974.

41. Bowditch, F.W. in letter to Eric O. Stork, EPA, June 4, 1974.

42. Yarrington, R.M. and W.E. Bambrick, "Deactivation of Automobile Exhaust Control Catalysts," J. Am. Poll. Control Assoc. XX (1970), 398.

43. Weaver, E.E. "Effects of Tetraethyllead on Catalyst Life in Customer Type Vehicle Operation," SAE Transactions LXXVIII (1969), Paper No. 690016.

44. Mooi, J., J.P. Kuebrick, M.F.L. Johnson, and F.L. Chloupek, "Modes of deactivation of exhaust purification catalysts," API Preprint No. 01-73, Philadelphia Meeting, 1973.

45. Gallopoulos, N.E., J.C. Summers, and R.L. Klimisch, "Effects of engine oil consumption on the activity of exhaust oxidation catalysts," SAE Meeting in Detroit, May 1973, (GMR-1371).

46. Shelef, M., R.S. Dalla Betta, J.A. Larson, et al., "Poisoning of noble metal monolithic oxidation catalysts in automobile exhaust environment," presented at the National AIChE Meeting, New Orleans, March 1973.

47. Hetrick, S.S. and F.J. Hills, "Fuel lead and sulfur effects on aging of exhaust emission control catalysts," SAE Paper No. 730596, May 1973.

48. Neal, A.H., E.E. Wigg, and E.L. Holt, "Fuel effects on oxidation catalysts and catalyst-equipped vehicles," SAE Paper No. 730593, Detroit, May 1973.

49. Holt, E.L., E.E. Wigg, and A.H. Neal, "Fuel effects on oxidation catalyst and oxidation systems II," SAE Paper No. 740248, Detroit, January 1974.

50. Data presented to the Panel of Consultants on Catalysts by Daimler-Benz A.G., May 21, 1974.

51. Data presented to the Panel of Consultants on Catalysts by Matthey-Bishop, June 27, 1974.

52. Data presented to J.W. Hightower by M. Gothelf, Gould Inc., in telephone conversation July 9, 1974.

53. Data presented to the Panel of Consultants on Catalysts by Volvo, May 23, 1974.

54. Southwest Research Institute, "A Literature Search and Analysis of Information Regarding Sources, Uses, Production, Consumption, Reported Medical Cases, and Toxicology of Pt and Pd," prepared for EPA, Contract No. 68-02-1274, April 15, 1974.

55. Data presented to the Panel of Consultants on Catalysts by Engelhard Industries, June 21, 1974; Pt Metals Rev. XVIII (1974), 64.

56. Data presented to the Panel of Consultants on Catalysts by Ford, May 29, 1974.

57. Voorhoeve, R.J.H., J.P. Remeika, P.E. Freeland, and B.T. Matthias, Science, (July 28, 1972), 353.

58. Harris, W.J. and N.B. Hannay, "Trends in Usage of Rare Earths," NMAB Report 266, October 1970.

59. Gauguin, R., M. Graulier, and D. Papee, "Properties required of catalyst carriers for exhaust gas purification," Am. Chem. Soc. National Meeting, Los Angeles, April 1974.

60. Data on U.S. production of alumina (8 million tons/year) supplied by W. Hayden, Martin Marietta, July 9, 1974.

61. Data submitted to NAS Medical Biologic Effects of Environmental Pollutants, Platinum Group Metals Panel, by General Motors, March 8, 1974.

62. Beltzer, M., R.J. Campion, and W.L. Peterson, "Measurement of vehicle particulate emissions," SAE Paper No. 740286, Detroit, March 1974.

63. Malanchuk, M., N. Barkley, G. Contuer, M. Richards, R. Salter, J. Burkart, and Y. Yang, "Exhaust Emissions from Catalyst-Equipped Cars," preliminary EPA report, March 1974.

64. Balgord, W.D., "Fine Particles Produced from Automotive Emissions-Control Catalysts," Science CLXXX (1969), 1168.

65. Roberts, A.E. "Platinosis - A Five Year Study of the Effects of Soluble Pt Salts on Employees in a Pt Laboratory and Refinery," Arch. Indust. Hyg. & Occ. Health IV (1951), 549.

66. Treedman, S.O. and J. Krupey, "Respiratory Allergy Caused by Pt Salts," J. Allergy XLII (1968), 233.

67. Data presented by R.M. Clyne and W.V. Andresen, American Cyanamid Company, March 5, 1974.

68. Wood, J.M. "Biological Cycles for Toxic Elements in the Environment," Science CLXXXIII (1974), 1049.

69. Jensen, S. and A. Jernelov, Int. At. Energy Agency Tech. Report Ser. 137 (chapter 4), 1972, p. 43.

70. Sax, N.I. Dangerous Properties of Industrial Materials. 2d Ed. Reinhold Pub. Co., 1973.

71. Moran, J.B. "Assuring public health protection as a result of the mobil source emissions control program," SAE Paper in Detroit, February 1974.

72. Report to EPA by General Motors, "Regarding Automotive Sulfate Emissions: A Status Report," May 7, 1974.

72a. Moran, John B. "Review of Comments on Automotive Sulfate; Federal Register Notice, Second Draft," Sept. 5, 1974.

72b. Redmond, John Jr., (National Research Council) in letter to Joe W. Hightower, August 2, 1974.

72c. Lewis, T.R., M.O. Amdur, M.D. Fritzhand, and K.I. Campbell, "Toxicology of Atmospheric Sulfur Dioxide Decay Products," EPA Publication AP-III, July 1972.

73. Phillips, P. British Patent 6,096, 1831.

74. Lee, S.D., V.N. Finelli, L. McMillian, and R.M. Danner, "Biochemical Effects of Emissions from an Automobile Engine with and without Catalytic Converter," Preliminary EPA report, March 1974.

74a. Treou, J.F. et al., AMA Arch. Ind. Hyg. Occup. Med. 2, 716(1950).

75. Schlatter, J.C., R.L. Klimisch, and K.C. Taylor, Science CLXXIX (1973), 798.

76. Skyarov, A.V., I.I. Tretyakov, B.R. Shub, and S.Z. Roginski, Doklad. Akad Nauk. SSSR CLXXXIX (1969), 1302.

77. Bond, G.C. Catalysis by Metals, Academic Press, 1962, p. 461.

78. Carberry, J.J. and J.B. Butt, Catal. Revs. Sci. and Eng. (in press).

79. Brittain, M.I., Ph.D. Dissertation, Yale University, New Haven, Conn., 1967.

80. Shelef, M. and J.T. Kummer, Chem. Eng. Progress Symposium Series No. 115, LXVII (1971), 74.

81. Peters, M.S. AEC TID-18423, 1963.

82. Ayen, R.J. and Y.-S. Ng. Inter. J. Air & Water Poll. X (1966), 1.

83. Ayen, R.J. and M.S. Peters, IEC Proc. Design Devel. I (1962), 205.

84. London, J.W. and A.T. Bell, J. Catal. XXXI (1973), 32.

85. Unland, M.L. J. Catal. XXXI (1973), 156.

86. Kobylinski, T.P. and J.B.W. Taylor, J. Catal. (in press).

87. Amirhazmi, A., J.E. Benson, and M. Boudart, J. Catal. XXX (1973), 55.

88. Hegedus, L.L. GMR-1394, May 16, 1973; GMR-1571, March 29, 1974; _____ and Baron, GMR-1584.

89. Masamune, S. and J.M. Smith, AIChE J XII (1966), 384.

90. Heck, R.H., J. Wei, and J.R. Katzer, "The transient thermal response of a monoloth catalyst support," Inter. Symp. in Chem. Reaction Eng., Evanston, Ill., August 1974.

91. Young, L.C. and B.A. Finlayson, "Mathematical modeling of the monolith converter," Inter. Symp. in Chem. Reaction Eng., Evanston, Ill., August 1974.

92. Finalyson, B.A. "Modeling Monolith Converters," Cat. Revs., Sci. and Eng. (in press).

93. Young, L.C. and B.A. Finlayson, Paper given at AIChE Philadelphia Meeting, November 1973.

94. Hegedus, L.L. Paper presented at Am. Chem. Soc. National Meeting, Chicago, August 1973.

95. Wei, J. and R. Becker, "The optimum distribution of catalytic material on support layers in automotive catalysts," paper presented at the Am. Chem. Soc. National Meeting, Los Angeles, April 1974.

96. Johnson, W.C. and J.C. Chang, SAE Paper No. 740196, 1974.

97. Carberry, J.J. and A.A. Kulkarni, J. Catal. XXXI (1973), 41.

APPENDIX A

Companies Site-Visited or Interviewed

1. Domestic

a. Ford Motor Company Dearborn, Michigan	May 6, 1974	*Hightower, Ollis, Butt, Wise
b. Chrysler Corporation Detroit, Michigan	May 6, 1974	Hightower, Ollis, Butt, Wise
c. General Motors Corporation Warren, Michigan	May 7, 1974	Hightower, Ollis, Butt, Wise
d. Engelhard Industries Murray Hill, New Jersey	June 10, 1974	Hightower, Ollis, Butt
e. Air Products and Chemicals Marcus Hook, Pennsylvania	June 6, 1974	Ollis
f. Oxy-Catalyst West Chester, Pennsylvania	June 11, 1974	Ollis
g. Union Oil Co. of California Brea, California	April 2, 1974	Hightower, Wise
h. American Oil Company Whiting, Indiana	March 28, 1974	Hightower
i. E.I. duPont de Nemours Wilmington, Delaware	June 12, 1974	Ollis
j. Universal Oil Products Des Plaines, Illinois	May 16, 1974	Butt
k. Clyde Engineering Service (meeting in Evanston, Ill.)	May 20, 1974	Butt
l. Questor Corporation Toledo, Ohio	June 12, 1974	Hightower, Butt
m. Gulf Research and Development Pittsburgh, Pennsylvania	June 5, 1974	Butt

*Last names of the members of the Panel of Consultants on Catalysts making visits.

APPENDIX A (continued)

1. Domestic (continued)

n.	Bell Laboratories Murray Hill, New Jersey	June 7, 1974	Ollis
o.	Corning Glass Works Corning, New York	June 5, 1974	Ollis
p.	Exxon Research and Engineering Linden, New Jersey	June 3, 1974	Ollis
q.	Gould, Incorporated Cleveland, Ohio	June 13, 1974	Hightower, Butt

2. Nondomestic Companies Interviewed at CMVE Meeting in Washington May 21-24, 1974 by Butt or Ollis

a. Daimler-Benz AG
b. Fiat, S.p.A./Ferrari
c. Honda Motor Company
d. Nissan Motor Company, Ltd.
e. Adam Opel AG
f. Peugeot, Inc.
g. Regie Nationale Des Usines Renault
h. Saab-Scania Aktiebolag
i. Toyo Kogyo Company, Ltd.
j. Toyoto Motor Company, Ltd.
k. Volkswagenwerk AG
l. AB Volvo

APPENDIX B

General Questions to Companies from the Members of the Panel of Consultants on Catalysts of the Committee on Motor Vehicle Emissions

One or more members of the Panel of Consultants would like to visit your company to discuss the current status of the technological feasibility of using catalysts to control automobile emissions. Please be prepared to discuss the following general areas, and supply data supporting your statements. We realize that other panels of consultants may have requested similar information; in such cases where you have nothing new to add, please include a copy of or cite your previous responses. Also, please feel free to provide additional information not specifically mentioned that you think would help us fulfill this mission. If you have no data in a specific area, so indicate.

1. System - What catalytic systems are being considered currently for the removal of (a) HC and CO, and (b) NO_x?

2. Composition - What are the chemical components and compositions of your most promising oxidation and reduction catalysts? For various engines sizes could you specify reactor volume, maximum space velocities, and operating temperatures? What is the weight loading of active components? What is the composition of the support material and/or washcoat?

3. Physical Form - Are the emission-control catalysts in the form of pellets, monoliths, expanded metal screens, metal sponges, etc.? What advantages does the preferred physical form of the catalyst have over the others?

4. Reactor - What is the configuration of the container, and what measures are being taken to overcome attrition?

5. Durability - What are the durability limits under different driving conditions? What external conditions cause catalyst deactivation? Could you delineate the relative contribution of fuel and lubricant additives, over-temperature, to deactivation? Is any operating information available about effective operational windows and the results of excursions from these windows (temperature, space velocity, gas composition, etc.)? After exposure to a given quantity of leaded gasoline, what conditions are required for complete or partial recovery of a given catalyst? Is there

APPENDIX B (continued)

5. Durability (continued)

any indication of synergistic effects caused by various catalyst poisons?

6. Performance - Could a summary of data be obtained on the performance of catalysts in terms of conversion, light-off temperature, and physical deterioration with mileage?

7. Health Hazards - Discuss the effects of catalysts on emissions of polynuclear aromatics, partially oxidized compounds, SO_x, etc. Has any catalyst loss been observed and if so, to what extent, and in what physical and chemical form? Have any toxicological studies been performed on particulate matter issuing from catalyst exhaust systems? Provide information about the sulfate problem.

8. Activity Monitoring - What methods are being considered for monitoring the activity of the emission-control catalysts; i.e., the degree of deactivation? Are accelerated aging tests available for evaluation of catalyst performance? If catalysts are guaranteed for a given mileage, what factors would void the guarantee and how will these factors be assessed?

9. NO_x Standard - What catalytic systems currently meet the 0.4 g/mi NO_x standard? What solutions are being considered to the problem of ammonia formation? Can the reduction catalysts under consideration withstand exposure to an oxidizing atmosphere? What is the fuel economy penalty required to meet the current NO_x standard? All factors considered (system complexity, expense, durability, performance, fuel economy, as well as emission control), what in your opinion is a "reasonable" NO_x standard and why?

10. Three-Way Catalysts - What is the present development stage of a single catalyst for simultaneous control of HC, CO, NO_x? What are the operational windows for such conversion? What additional hardware is required to make these catalysts effective?

11. Mathematical Models - Do you have working mathematical models that accurately describe the performance of the catalytic systems (kinetics, diffusion, temperature, poisoning, etc.)? How do the various kinetic parameters change as the catalyst is poisoned?

12. Catalyst Supply - Do you foresee any problems associated with supply of catalytic material? Where will the noble metals come from, and is the mining capacity sufficient? Is recycling of deactivated catalysts being considered feasible at this time?

APPENDIX B (continued)

13. Anything Else Relative to Automobile Catalysts Not Already Covered.